# ACETATE SILK
## AND ITS DYES

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BY

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WITH A FOREWORD

BY

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## PREFACE

In view of the constantly increasing volume of technical literature upon all branches of industry, it hardly appears necessary to find an excuse for a book upon a subject of such wide interest as acetate silk, upon which there has been no previous specific treatise. The present volume is largely, but not entirely, based upon two series of articles, "Dyeing Acetate Silk" and "Acetate Silk, Its Dyes And Their Application," originally written especially for, and published in, the *American Dyestuff Reporter* of 1925 and 1926.

Some additional papers under various titles were later published in the *Textile Colorist* and the *Canadian Colorist and Textile Processor*. The information presented in these papers was collected from every available source, and very little of it was original. In the present volume this material has been rewritten, revised, corrected, and enlarged to include all information available at the time of completing the manuscript.

The author has no hope that all who peruse this volume will at once be able to obtain all of the desired results on the various forms of acetate silk, and has merely endeavored to bring the available and rather widely scattered information on this subject into a concise and convenient form for the busy chemist, dyer, and textile technologist. Dyeing is not learned from books alone, but it is hoped that the present volume may aid the busy mill man to make such experiments as will enable him to solve his own problems on dyeing acetate silk. After all, the really successful dyer is the man who can take an idea, work it out, and apply it to his own problems.

### *Acknowledgment*

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president of the Lustron Company of Boston, Mass., who very kindly consented to review the entire manuscript. Mr. Mork was co-inventor of the first patented process for the manufacture of acetate silk and himself developed many of the manufacturing, early dyeing, and other processes used in connection with this fiber. He has been connected with this industry longer than any other one man and is a leading authority on both acetate silk and the methods of handling it. His suggestions, corrections, and information have been most valuable in finishing up the manuscript.

Among the many others who deserve special credit and thanks are:

Dr. Louis A. Olney, Professor of Chemistry and Dyeing at Lowell Textile School, who, as Editor of the *American Dyestuff Reporter,* edited all of the original papers by the author on acetate silk, and who in this work, as in all other, has been most kind and considerate with his help and encouragement.

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# INTRODUCTION

By Dr. Louis A. Olney

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LUSTER as a desirable quality of textile materials has been prominently before the purchasing public for several thousand years. During most of this period dependence has been placed upon natural silk for the purpose of producing it, but the past half century has witnessed an interesting, and we might say, revolutionary encroachment upon the domain of the silk worm.

The luster produced upon cotton yarn and cloth by subjecting it, under tension, to the action of concentrated caustic soda solution (mercerization) has been and is still a very important factor in the production of beautiful textile materials, but the luster produced in this manner has not been nearly as great or its development and use so spectacular as that of the so-called artificial silks, which in many instances far exceed in luster the natural silks.

These extremely lustrous fibers have all been produced in a manner which imitates the silk worm, as far as mechanism of process is concerned, but chemically they are entirely different; and the final fiber substance is not at all comparable with true silk in composition. For this latter reason they are not, strictly speaking, artificial silks. As a consequence of this misnomer, various attempts have been made to devise a generic name which would not convey an erroneous idea, but which could properly be used to designate any type of fiber produced by forcing a semi-liquid substance through a very fine orifice, with subsequent hardening. Among the names suggested, that of "Rayon" appears to have met with the greatest favor, and at the present time it is being quite generally used by both textile manufacturer and consumer.

From a chemical point of view the artificial silks or rayons may be classified into two distinct groups: those which are in reality regenerated celluloses, and those in which the final fiber substance is a cellulose ester. The former group is typified by the Nitro,

Cupro Ammonium and Viscose Silks, while the latter, up to the present time, is represented only by the Cellulose Acetate Silks. The manufacturers and distributors of the acetate silks have been somewhat loath to adopt the term "Rayon" since their product is in some respects so different from the regenerated celluloses. This in a way is unfortunate since, to some extent, it defeats the honest endeavor that has been made to secure a simple word which could be used to designate any fiber produced by the above mentioned mechanical process, regardless of the chemical reactions involved. Repudiation of the term "Rayon," however, does not change the fundamental situation, and cellulose acetate products still remain, as much as ever, in the category of "Artificial Silks."

The extensive commercial use of the acetate silks was somewhat delayed, owing to the difficulties at first experienced in producing upon them full dyeings and fast colors. Failures in this respect were simply the natural consequence of attempts made to apply to these acetate silks the same dyes by the same methods as had formerly been found so satisfactory with the regenerated cellulose silks which were so readily dyed by practically all of the methods used for the dyeing of cotton. It was not until the marked difference between the dyeing properties of cellulose acetate and cotton were fully appreciated, and dye chemists recognized the fact that entirely new dyes and dyeing processes might have to be devised, that any great headway was made toward the satisfactory dyeing of acetate silk. The last five years have witnessed remarkable developments in this respect, and many dyes of entirely new molecular structure, as well as new processes of application, have been devised to overcome obstacles which at one time threatened disaster to the future of the acetate silk industry. It is doubtful if any of the many remarkable developments which have been made in connection with color chemistry and dyestuff application illustrate more vividly the ability of the textile and color chemist to contend with the most puzzling of problems, when the exigency arises.

Notwithstanding the remarkable developments that have been made in the dyeing of acetate silk, there is still much work to be done in order that the dyer may be able to color this fiber with the

same ease, flexibility, and wide range of colors that may so easily be applied to cotton.

In this volume, Mr. Mullin has presented in a comprehensive manner the history of the remarkable development of acetate silk dyeing and has described with detail the processes which are now in use for this purpose.

While much of the material presented in this volume is necessarily a record of the work of other investigators, the author has frequently introduced to advantage the results of his own investigation and specialized knowledge. Being a thoroughly trained textile chemist, familiar with the underlying principles of the subject at hand, he has avoided the vaguesness of expression and technical ambiguities which often appear in books of this character.

To all those who are interested in the dyeing of cellulose acetate silk, this book not only will be found valuable as a reference book, but also will serve as a textbook for those who wish to make a comprehensive study of the subject.

# CHAPTER I

## GENERAL CONSIDERATIONS

ACETATE SILK, the infant prodigy of the textile industry, by reason of its new, valuable, and extremely interesting chemical, physical, textile, and dyeing properties, has practically forced itself upon the attention of every branch of textile manufacturing. Without doubt the unique dyeing properties of this fiber are foremost in its favor at the present time, for while it offers many other and very interesting points for its support, no other fiber can even approach it for most white or two-color effects when in combination with the older and better known fibers.

At the present time all of the rayons[a] are in unprecedented demand, but acetate silk by reason of its dyeing porperties alone, holds a certain definite field of usefulness upon which none of the older rayons (nitro, viscose and cuprammonium) can even encroach. Yet only a few years ago it was these very dyeing properties, or rather with the information then available, its lack of dyeing properties, that restricted the use of this wonderful new fiber. The fact that both the fiber and its dyeing methods, as well as most of the dyestuffs themselves, are very new, the two latter having been developed especially for this particular fiber, renders technical information on these subjects of special interest, especially to all textile chemists and dyers, at this time.

We are all more or less familiar with the older varieties of regenerated cellulose rayon which have come into such wide use in recent years, their individual and collective properties, methods of

[a]The name rayon has been applied as a class designation to the whole group of fibers formerly known as artificial silks. However, as pointed out by Davies, *American Dyestuff Reporter 15,* 197 (1926), this does not satisfy the technical mind, since the fibers produced by the different chemical methods possess different chemical, physical, and dyeing properties. It is therefore customary for the technical man to refer to the different rayons under the various names which describe the chemical processes involved in their manufacture, and he therefore speaks of viscose silk, cuprammonium silk, nitro silk, and cellulose acetate silk, acetyl, or acetate silk, as we will call it.

dyeing, etc. Acetate silk is an entirely different product in that it is a cellulose ester (acetate) and not a regenerated, modified, or hydrated form of cellulose, as are the older and better known rayons. There is no more relation between the older rayons and acetate silk in many of their properties than there is between glycerol and olive oil, or alcohol and ethyl acetate. In this instance we may compare the older rayons to the gylcerol and the olive oil to acetate silk. Cellulose is the basic constituent of all of our present rayons, acetate silk included; but in the acetate silk the cellulose is combined with acetic acid to form an ester, just as in olive oil the glycerol is combined with the fatty acids to give the ester which we know as olive oil. With this in mind, we would expect quite different properties in the new product, acetate silk, and we are certainly not disappointed. No dyer or chemist would attempt to successfully substitute glycerol for olive oil, or alcohol for ethyl acetate, in very many processes, or *vice versa*. No more can he with uniform success dye acetate silk by the methods successfully applied to the older rayons or cotton.

The original Chardonnet silk was also an ester (cellulose nitrate), and had some properties in common with the acetate silk, but as this original Chardonnet silk was very flammable, one of the first improvements was a method of rendering it non-flammable, by denitrating it. This denitration changed it from an ester to a hydrated cellulose, which chemically corresponds to the present Chardonnet or nitro silk. The fact that acetate silk differs so much from the older rayons in constitution and most of its properties necessitates a much more detailed discussion of the subject of dyeing than would be desirable in the case of a fiber more nearly related to a known commercial product, in order to give the dyer a full and complete understanding of the subject.

### *The Results of Research*

Within the last five years, research upon dyes and dyeing methods for acetate silk has possibly developed more new facts and theories upon dyes and dyeing, as well as absolutely new classes of dyestuffs, than any other research along similar lines since the development of the vat dyes.

Some of these new products are the Ionamines, the "dispersol"

and "sulfato" dyes, etc. All of these will be considered later in due order. Many of these new dye stuffs have no other use than upon acetate silk, but the research, theories, and new products are already having an effect upon the dyes for, and the methods of application to, the older rayons and natural fibers.

At the same time, the combined research upon the rayons (collectively) has enormously increased our knowledge of cellulose and related compounds, much to the advantage of the whole textile industry, as well as of many others. Sad to relate, the advances in the field of our protein fibers, wool and silk, have not kept pace with that of cellulose. It is significant to note that most of these advances and discoveries have been made in England, where they appear to have very well learned the value of research.

TABLE I

DOMESTIC RAYON PRODUCTION BY THE PRINCIPAL AMERICAN COMPANIES

| *Company* | *Production in Pounds* | | | |
|---|---|---|---|---|
| | *1925* | *First 8 Mo. 1926* | *Total 1926 (Estimated)* | *1927 (Estimated)* |
| The Viscose Co. | 35,000,000 | 25,000,000 | 37,000,000 | 45,000,000 |
| Du Pont Rayon Co. | 6,761,560 | 6,900,000 | 11,500,000 | 15,500,000 |
| Tubize Art. Silk Co. | 5,200,000 | 5,000,000 | 7,000,000 | 8,000,000 |
| Industrial Rayon Corp. | 2,250,000 | 2,250,000 | 3,500,000 | 4,000,000 |
| American Cellulose & Chemical Mfg. Co. | 1,500,000 | 1,500,000 | 2,500,000 | 3,500,000 |
| Belamose Corp. | 675,000 | 650,000 | 1,000,000 | 1,500,000 |
| Acme Art. Silk Co. | 322,665 | 250,000 | 400,000 | 500,000 |
| Other Firms | 500,000 | 350,000 | 500,000 | 2,500,000 |
| Total | 52,209,225 | 41,900,000 | 63,400,000 | 80,500,000 |
| | | *Acetate Silk* | | |
| | *1924* | *1925* | *1926* | *1927* |
| Celanese | | 1,500,000 | 2,500,000 | 3,500,000 |
| Lustron | 500,000[b] | 500,000[b] | 500,000[b] | ——— |

*Textile World 68*, 1749-50 (1925); *69*, 839 (1926); *70*, 1996 (1926).

[b]As estimated by *Textile World;* correct figures not available.

TABLE II

RAYON PRODUCTION IN POUNDS BY YEARS

| | *World* | *United States* |
|---|---|---|
| 1914 | 26,000,000 | |
| 1918 | 35,000,000 | |
| 1919 | 40,000,000 | |
| 1920 | 50,000,000 | 9,000,000 |
| 1921 | 65,000,000 | 18,000,000 |
| 1922 | 79,738,000 | 26,000,000 |
| 1923 | 97,000,000 | 35,500,000 |
| 1924 | 141,414,000 | 38,750,000 |
| 1925 | 185,000,000 | 52,200,000 |
| 1926 (Estimated) | 210,000,000 | 63,400,000 |

*Textile World, 68*, 1749-50 (1925); *70*, 1997 (1926).

TABLE III

WORLD RAYON PRODUCTION BY COUNTRIES

| Country | Production 1922 | 1923 | 1924 | 1925 |
|---|---|---|---|---|
| United States | 23,500,000 | 35,400,000 | 39,000,000 | 52,200,000[c] |
| England | 15,340,000 | 16,500,000 | 23,947,000 | 28.000,000 |
| Germany | 12,584,000 | 13,000,000 | 23,672,000 | 27,100,000 |
| Italy | 6,292,000 | 10,000,000 | 18,480,000 | 30,000,000 |
| France | 6,292,000 | 7,700,000 | 12,333,200 | 14,400,000 |
| Belgium | 6,292,000 | 6,000,000 | 8,874.800 | 11,100,000 |
| Switzerland | 1,887,600 | 3,700,000 | 4,0C4,000 | 5,500,000 |
| Holland | 2,516,800 | 2,600,000 | 3,366,000 | 4,400,000 |
| Austria | 1,573,000 | . | 2,640,000 | 3,500,000 |
| Poland | 943,800 | | 1,540,000 | 2,200,000 |
| Czechoslovakia | 629,200 | | 1,293,600 | 2,000,000 |
| Japan | | | 1,199,000 | 1,400,000 |
| Hungary | 1,887,600 | | 616,000 | 700,000 |
| Spain | | | 184,800 | 220,000 |
| Sweden | | | 176,000 | 176,000 |
| Russia | | | 88,000 | 88,000 |
| Other Countries | | 2,100,000 | | |
| Total | 79,738,000 | 97,000,000 | 141,414,400 | 182,984,000 |

[c]Recent statistics from the U. S. Bureau of Census give 51,800,000 pounds for 1925.

TABLE IV

THE PERCENTAGE CONSUMPTION OF THE RAYONS BY THE VARIOUS TEXTILE INDUSTRIES

| *Industry Year* | *1912* | *1915* | *1918* | *1920* | *1921* | *1922* | *1923* | *1924* | *1925* |
|---|---|---|---|---|---|---|---|---|---|
| Hosiery | 30 | 65 | 40 | 25 | 23 | 24 | 22 | 23 | 28 |
| Knit Goods | 7 | 5 | 17 | 21 | 29 | 26 | 25 | 14 | 5 |
| Silk | 10 | 5 | 18 | 13 | 12 | 11 | 15 | 18 | 16 |
| Cotton | 10 | 15 | 13 | 10 | 9 | 10 | 11 | 15 | 26 |
| Underwear | — | — | — | 1 | 2 | 4 | 5 | 11 | 13 |
| Braids | 10 | 2 | 5 | 14 | 10 | 11 | 10 | 8 | 4 |
| Upholstery | 3 | 2 | 2 | 2 | 2 | 2 | 2 | — | — |
| Plush | 15 | 3 | 2 | 3 | 1 | 1 | 2 | 2 | 1 |
| Wool | 3 | 2 | — | 1 | 1 | 1 | 1 | 1 | 1 |
| Miscellaneous | 12 | 1 | 3 | 10 | 11 | 10 | 7 | 8 | 6 |

# CHAPTER II

## THE DEVELOPMENT OF RAYON

THE credit of first suggesting an artificial silk is usually given to Reaumur (1734) but recent[1] information indicates that this rightly belongs to Robert Hooke, author of "Hooke's Micrographia" (1665). Undoubtedly Reaumur also suggested artificial silk. The following quotations are from page 7 of Hooke's book.

"A conjecture, that it may perhaps be possible to spin a kind of artificial Silk out of some glutinous substance that may equalize natural Silk."

"A pretty kind of artificial Stuff I have seen, looking almost like transparent Parchment, Horn or Ising-glass, and perhaps some such thing it may be made of, which being transparent, and of a glutinous nature, and easily mollified by keeping in water, as I found by trial, had imbib'd, and did remain ting'd with a great variety of very vivid colours, and to the naked eye it looked very like the substance of Silk. And I have often thought, that probably there might be a way found out, to make an artificial glutinous composition, much resembling, if not full as good, nay better, than that Excrement, or whatever other substance it be out of which, the Silk-worm wire-draws his clew. If such a composition were found, it were certainly an easie matter to find very quick ways of drawing it out into small wires for use. I need not mention the use of such an invention, nor the benefit that is likely to accrue to the finder, they being sufficiently obvious. This hint therefore, may, I hope, give some Ingenious inquisitive Person an occasion of making some trials, which if successful, I have my aim, and I suppose he will have no occasion to be displeased."

Schwabe of Manchester experimented on various processes for the production of an artificial silk in 1842 but the first patent on the subject appears to be that of Audemars of Lausanne, who in 1855 attempted to utilize an ether-alcohol solution of nitrocellulose, prepared by nitrating the bast fibers of the mulberry tree.

This effort was not successful but in 1882 and 1883, Powell, Weston, Swan, Swinburne, and Wyne worked out methods very similar to those later adapted by Chardonnet. Chardonnet had his first success in 1884 or 1885, but it was not until about 1890 that it was really a success, commercially. The British rayon industry may be said to date its existance from the work of Cross and Bevan on viscose in 1892.

### *Cellulose Acetate*

The first reference in the technical literature regarding the acetylation of cellulose appears to be that of Schuetzenberger[2] who heated cellulose in a closed tube with acetic anhydride. Worden,[3] in an excellent review and discussion of the art of preparing cellulose acetate up to 1919, divides the advances in the preparation of the ester into three periods:

1. *The academic period,* covering from the work of Schutzenberger in 1865 to that of Cross and Bevan in 1894.[a]
2. *The period 1894 to 1911,* important advances indicated by the Miles patents.[b]
3. *The period 1911 to 1919,* important advances indicated by the Dreyfus patents.

The early (1st period) methods of preparing cellulose acetate are of no particular interest at the present time. They are so ably covered by Worden[4] that it is useless to give them in detail here.

The next important development after Schuetzenberger's original work appears to be that of Franchimont,[5] who discovered the so-called catalytic action of sulfuric acid or zinc chloride in the acetylating reaction. That this discovery marked an important step is evident from the fact that even today most of the industrial methods of acetylating cellulose utilize sulphuric acid, in one form or another, as the catalytic agent.

The next important development in the field of cellulose acetate appears to be the patent of Cross and Bevan[a] which marks the

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[a]British Patent No. 9,676.
[b]United States Patents No. 838,350, etc.

beginning of Worden's second period in the development of the acetate. In this patent the industrial value and technical applications of cellulose acetate are mentioned for the first time.

Undoubtedly the most important development during the second period is covered by the patents of G. W. Miles, particularly his patents of 1905. Miles's early patents covered the direct acetylation of fibrous cellulose, United States Patent Application No. 24,575, dated June 23, 1900, which was allowed December 18, 1900, abondoned and then included in his application of May 27, 1901. His United States Patent No. 733,729 (1903) and Canadian Patent No. 90,848 (1905), while important, covered the production of cellulose acetates soluble only in expensive, toxic solvents, such as chloroform and tetrachloroethane.

His later discovery—covered by United States Patent No. 838,350 (1906), reissue 12,637 (1907), British Patent No. 19,330 (1905), French Patent No. 358,079, Belgian Patent No. 187,308 (1905), Hungarian Patent No. 35,866 (1905), Austrian Patent No. 41,461 (1909), Canadian Patent No. 103,045, and German Patent No. 252,706—covers a hydrating or hydrolyzing step in the preparation of cellulose acetate, wherein the chloroform soluble (primary) acetates are converted into acetone soluble (secondary) products. The German Patent covering this process was issued only after years of litigation and sale to the Bayer Company, who held German Application No. E—20,963, which was added to Miles's Application M-28,289, and covered by the one patent, No. 252,706. The value of this process lies in the solubility of the hydrolyzed product in comparatively cheap solvents, from which it gives filaments and films of good strength and flexibility. Many modifications of the original hydrating process have been patented, and described in the literature, e.g., British Patent No. 24,067 (1906); French Patents No. 371,447 (1906), and No. 428,554 (1910); etc.[e]

Worden's third period covers the first Dreyfus patents of July 5, 1911, British Patents No. 20,975, No. 20,976, and No. 20,977, etc. These patents cover the preparation of highly viscous cellu-

[e] The products of direct esterification, soluble in chloroform, are designated *primary acetates,* while the hydrolyzed, acetone-soluble products are *secondary acetates.*

lose acetates and there are certainly a number of them. They cover the entire range of cellulose acetate manufacture, including the solvents used, etc. The first of these patents points out that high viscosity, high tensile strength, and elasticity are complementary. The product is soluble in alcohol plus chloroform, or in acetone, but insoluble in chloroform alone.

The original patents upon the manufacture of acetate silk appear to be those issued to A. D. Little, W. H. Walker and H. S. Mork, the latter now vice-president of the Lustron Company. These were United States Patents No. 712,200 of 1902, and No. 792,149, June 13, 1905, which covered the use of cellulose acetate prepared according to United States Patents No. 709,922,[d] etc.

The scientific, technical, and patent literature from the time of Schuetzenberger up to the present, and particularly since the world war, is replete with references to research upon cellulose acetate, acetate silk, dyes for and dyeing methods, and related subjects. Worden[3,4] covers all of the important developments up to 1919, which are entirely too voluminous for the present available space. Since 1919 the bulk of literature upon this subject has increased tremendously and can best be reviewed by reference to the excellent abstract journals covering the various phases of chemical and textile technology.

Possibly Grandmonyeu was the first to prepare acetate silk in 1898, but the Lustron Company of Boston appear to have been the pioneers in the manufacture of acetate silk on a commercial scale, with Bayer and Company of Germany, and possibly the Société Chimique des Usines du Rhone of Lyons, France, founders of the "Rhodiaseta" Company, closely following. Henckle von Donnersmarck Artificial Silk and Acetate Works also appear to have investigated the field to some extent and probably manufactured some acetate silk. Undoubtedly many other firms at various times conducted work of a more or less experimental nature upon this process.

Acetate silk was produced in a small way by Dr. Camille and Dr. Henri Dreyfus in Basle, Switzerland, in 1910 to 1913. During the World War these investigators were called to England

[d] See page 26.

to handle the production of cellulose acetate for use in the preparation of aeroplane dopes. At the close of the war their attention was again given to the production of acetate silk, which resulted in the formation of British Celanese, Ltd., and associated companies[c] in various countries. Although the plants of this company in England had been the world's largest producers of cellulose acetate during the war, they did not start the production of the present Celanese until about 1918. In the early part of 1921, they were producing about 1000 pounds of Celanese daily but doubled their capacity during the year. Production has steadily increased up to date.

Celanese was produced in America on a small scale in 1919, and large-scale production was started in 1922, with a constant increase in capacity. Within the past few years Celanese has also been produced in both France and Belgium. One of the most recent developments in connection with Celanese appears to be the formation of a Canadian Company, the Canadian Celanese, Ltd., Dr. Camille Dreyfus, president, to build a $7,200,000 plant at Drummondville, Quebec, Canada.

Acetate silk has been manufactured for some years in France by the Société pour la Fabrication de la Soie "Rhodiaseta." This company was founded by the Comptoir des Textiles Artificiels and the Société Chimique des Usines du Rhone, the latter company having had some previous ten years' experience in the production of high grade, stable, cellulose acetate. While Rhodiaseta yarn does not appear to be very well known in America, it enjoys an excellent reputation and sale in France and neighboring countries. Acetate silk is also manufactured in Switzerland, and several other companies are either manufacturing or preparing to manufacture acetate silk.

[c]The American Cellulose and Chemical Company, Canadian Celanese, Ltd., La Celanese Francaise, and others.

*References*

[1] G. J. Alexander, *J. Soc. Chem. Ind. 45,* 221 (1926).
[2] P. Schuetzenberger, *Comp. rend. 61,* 485-6 (1865).
[3] E. C. Worden, *J. Soc. Chem. Ind. 38,* 370-4T (1919).
[4] E. C. Worden, "Technology of Cellulose Esters", Vol. VIII, 1916.
[5] A. Franchimont, *Comp. rend. 89,* 711 (1879) and *92,* 1053 (1881).

# CHAPTER III

## PREPARATION

*The Acetylation of Cellulose and "Catalysts" Used. "Ripening" the Acetate and Its Effect on Solubility. The Manufacture of Acetate Silk, Mixed Ester Fibers and Colored Acetate Silk.*

CELLULOSE acetate may be prepared from cellulose in various forms, such as cotton or suitably purified wood pulp, acetic anhydride, glacial acetic acid, and a so-called "catalyst"' or condensing agent, such as sulfuric acid (either alone or in some form of combination), phosphoric acid, zinc chloride, anhydrous acetates of zinc or manganese, etc. It is understood that in the present industrial processes, purified cotton linters or paper pulp is used as the basic material and, that sulfuric acid is almost or quite universally used as the catalyst.

From these simple starting materials, by suitable manipulation, it is possible to obtain, and is in fact frequently difficult to avoid obtaining, a wide variety of resulting products, differing very materially in their properties. These variations may start with the proportions and nature of the initial ingredients; the temperature and duration of acetylation; the time, temperature, and method of "ripening", etc., which to a large extent influence the acetate content of the resulting product; the method and extent of purification, etc. In the case of acetate silk, this variation may be even further complicated by the solvent used in spinning, the methods and mechanical apparatus for spinning, the nature of the spinning bath, if one is used, etc.

That wide differences in the properties of the finished products, both as cellulose acetate and acetate silk, do exist is fully recognized by all those familiar with the industry. An instance of this is the differences in our two best known acetate silks, Lustron and Celanese. Both of these types have acetylation values higher than cellulose diacetate and lower than the triacetate, but Lustron is more highly acetylated than Celansee.

In the manufacture of Lustron,[1] the cellulose acetate is dis-

solved in a combination of tetrachlorethane and some cheaper solvent, or in chloroform. This solution is forced through the spinneret into a hydrocarbon, such as kerosene, in which the solvent is dissolved and the cellulose triacetate (Lustron) fiber precipitated. In the manufacture of Celanese, on the other hand, the cellulose acetate is dissolved in acetone or a similar cheap, volatile solvent, and the fiber subsequently formed by the evaporation of the solvent. Most dyers soon become familiar with the differences in the two products, which will be considered more in detail as we proceed.

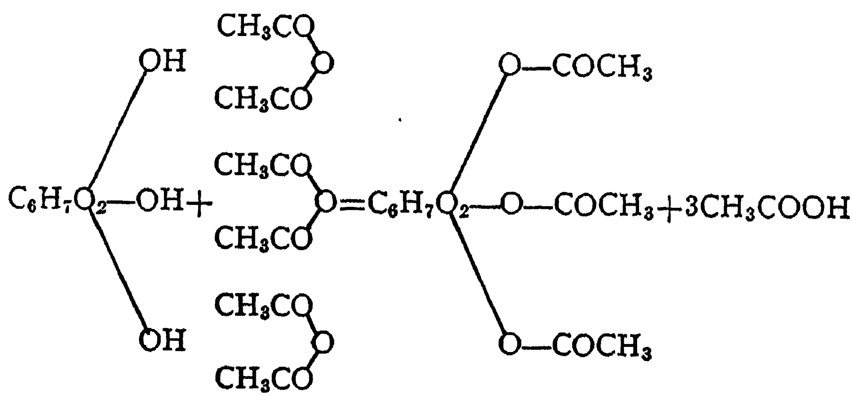
In order that we may have a better understanding of the whole subject as just outlined and its relation to the dyeing and other processes on acetate silk, more details regarding the preparation of the cellulose acetate may be of interest.

### *Acetylation*

Heuser[2] states that cellulose triacetate is formed according to the equation:

$$C_6H_{10}O_5 + 3(CH_3CO)_2O = C_6H_7O_5(CH_3CO)_3 + 3CH_3COOH;$$

or, written in another manner:




Cellulose Cellulose Triacetate.

While all readers may not agree as to the exact formula for cellulose, the above serves very well to illustrate the principal of the reaction. Theoretically, according to this equation, 100 grams

of air-dry cellulose, such as cotton containing 5 or 6 per cent of water, will require 188 grams of absolute acetic anhydride. However, in practice an excess of the anhydride, or 250 to 400 grams, per hundred grams of cellulose, are used, according to process.

From the above equation we see that in the preparation of cellulose triacetate, all three of the hydroxy groups are esterified. Theoretically, the mono- and di-acetates of cellulose are also possible, but it is somewhat doubtful if these are prepared commercially, except by hydrolysis. Frequently the process which should yield these lower acetates by direct acetylation results in a mixture of cellulose triacetate and various lower acetates, with unacetylated cellulose. Celanese contains only about two acetate groups per cellulose molecule and therefore corresponds closely to cellulose diacetate; but it is undoubtedly produced by hydrolysis, as will be explained under the Miles process and patents.

Deschiens[3] divides the processes for manufacturing cellulose acetate into two groups: (*a*) those in which the cellulose acetate dissolves; and (*b*) those in which it does not pass into solution. The *a* processes include those covered by the Miles patents, the Usines due Rhone, and most of the Dreyfus patents. Some of the Dreyfus patents also cover the *b* type of process, which does not appear to have a very extensive commercial use at this time.

Cross and Bevan in 1894 received the first patent upon the manufacture of cellulose acetate, British Patent No. 9,676. This patent claims a compound of cellulose with zinc acetate, which is prepared by mixing cellulose hydrate (obtained by various known processes, such as precipitating the solution of cellulose in zinc chloride, or in cuprammonium solution, or by acting on cellulose with sodium hydroxide and carbon disulfide) with zinc acetate. The cellulose hydrate from about 100 parts of dry cellulose is mixed with 150 parts of crystallized zinc acetate in solution, and the mixture is evaporated and dried at 100° C. The second claim in this patent is for an acetate of cellulose, prepared by treating the zinc acetate cellulose compound in a finely powdered state with acetyl chloride, the temperature not being allowed to rise above 30° C. (86° F.). Two molecules acetyl chloride are used for each one of zinc acetate in the compound.

The product is washed with water and dried. It may be purified by treatment with chloroform, which dissolves the cellulose acetate, leaving any unacetylated cellulose undissolved. They compared this product with cellulose nitrates and state that from its solution in chloroform it may be obtained in transparent films or sheets and so used as a substitute for collodion, as a special varnish, etc. They also mention that it has the property of uniting with oils in suitable solvents of both, and holds the oils in such a way as to give films of a much softer texture without any loss of transparency. This patent is the first suggestion of a practical use for cellulose acetate to appear in the literature.

United States Patent No. 709,922 (September 30, 1902), British Patent No. 20,666 (September 22, 1902), and French Patent No. 324,862 (September 30, 1902) to A. D. Little, H. S. Mork, and W. H. Walker, have been stated to cover the cellulose acetate first used for the production of acetate silk (Lustron) in America. These patents specify the treatment of cellulose with acetic anhydride in the presence of an aromatic sulfonic acid, with or without the addition of a salt of that acid. For example, 100 parts of cellulose are treated with 350 parts of acetic anhydride. 5 parts of phenolsulfonic acid, and 5 parts of the sodium salt of phenolsulfonic acid. The reaction is effected at about 80° C. Naphtholsulfonic acid may also be used. The object of the sodium salt is to insure the absence of any free sulfuric acid.

The foregoing patents possibly exemplify the early types of cellulose acetates which, in the form of acetate silk were widely described in the literature as almost impossible to dye. These products were soluble only in chloroform and other expensive solvents. The later hydrolyzed products, as first disclosed in German Patent No. 252,706 to the Bayer Company and related patents to Miles, are soluble in acetone, mixtures of acetone with alcohol, or in extreme instances in water alone.[a] No doubt most of the present acetate silks are made from cellulose acetates prepared by the hydrolytic process. It would be interesting to compare the dyeing

[a] The chloroform soluble, acetone insoluble products of the direct acetylation of cellulose are designated *primary acetates,* while the acetone soluble product resulting from the hydrolyzing or "ripening" process are called *secondary acetates.*

properties of acetate silks prepared by these two different processes, with the new special dyes for acetate silk.

*Later Methods*

According to Deschiens[3] the present processes for the preparation of cellulose acetate may be divided into five steps: (1) The acetylation of the air-dry cellulose by acetic acid and acetic anhydride in the presence of sulfuric acid (or other chemical compounds), which acts as a "catalyst." (2) Hydrolysis, by adding water and acetic acid, taking care to avoid precipitation of the acetate. (3) Ripening, during which the product is left for a period of time, usually for at least 12 hours, at a fixed temperature, which varies in different processes and patents. The reaction thus continues regularly until the desired stage is reached. The duration and temperature of this ripening process have an important effect on the solubility and other properties of the resulting product. (4) Precipitation of the acetylated cellulose as a white flaky mass by the addition of a large excess of cold water containing sufficient alkali carbonate to neutralize the sulfuric acid. (5) Washing, centrifuging, and drying at 20 to 30° C. (68 to 86° F.) in well-ventilated rooms.

A very brief consideration of the above steps, even by a layman, will suffice to show that it is possible to alter the properties of the final product without difficulty. In fact, in actual commercial practice, it has been found extremely difficult to avoid the production of variable products, from day to day or even batch to batch. The production of an absolutely uniform product at all times requires a very close control of all factors and variables, which is possible only with the best equipment and skilled attention at all times. As in all other rayons, this feature of uniformity of product is of the utmost importance and forms the principal basis of superiority of different brands over other less uniform products.

According to the Miles patents, as exemplified by German Patent No. 252,706, to the Bayer Company, 100 parts of dry, scoured cellulose (preferably bleached cotton) is treated at a temperature below 40° C. (104° F.) with a mixture of 270 to 310

grams of acetic anhydride, 390 to 410 grams of glacial acetic acid, and 3 to 9 cubic centimeters of concentrated sulfuric acid, until the cellulose is disintegrated to form a white, nontransparent, pasty mass, the temperature being allowed to rise to 50° C. (122° F.). As the reaction is exothermic, the temperature is controlled by refrigeration. When the temperature begins to fall, the reaction vessel is warmed to 50 or 55° C. (122 to 131° F.) and held at this temperature for 36 to 40 hours or until the mass becomes more or less transparent, less viscous, and the cellulose is apparently in solution, forming a heavy, nearly transparent, light brown mass. A test portion is removed, precipitated in a large bulk of water, washed neutral, and dried, when it should be completely soluble in alcohol-free chloroform, but practically insoluble in absolute acetone. At this point the acetate is ready for the hydrolyzing or hydrating or ripening process.

A mixture of 60 or 65 cubic centimeters of water and 60 cubic centimeters of glacial acetic acid, per 100 grams of original cellulose, is added slowly to the cellulose acetate solution while stirring vigorously to avoid precipitation. This mixture is held at 40 to 50° C. (104 to 122° F.) for 12 to 16 hours, or until a precipitated, washed and dried sample is only plastic in warm chloroform but entirely soluble in pure acetone. The entire mass is then precipitated by pouring it into cold water, washed until neutral, and dried at 35 to 40° C. (95 to 104° F.). The yield from 100 grams of cellulose is 130 to 145 grams of partially hydrated cellulose acetate.

The resulting white, fibrous mass of secondary cellulose acetate is soluble in formic or acetic acids with some difficulty; readily soluble in tetrachlorethane, acetone, chloroform containing alcohol; less soluble in ethyl acetate, nitrobenzene and pyridine. It is insoluble in water, ethyl or amyl alcohol, amyl acetate, carbon tetrachloride, benzine, benzene, toluene or xylene. It is plastic in hot chloroform; soluble in hot 70 per cent aqueous ethyl alcohol from which it gelatinizes on cooling; plastic in glycerol at 125° C.; and soluble in a mixture of hot ethyl alcohol and benzene from which it is precipitated on cooling.

As an example of the early Dreyfus patents and methods, French Patent No. 478,023 (1914) to H. Dreyfus serves very well. A

hundred kilograms of cellulose (cotton or paper) containing 3 to 6 per cent of moisture are stirred into an acetylating bath at 0° C. (32° F.) containing a mixture of 300 to 400 kilograms of glacial acetic acid, 250 kilograms of acetic anhydride, and 10 to 15 kilograms of sulfuric acid. The temperature soon rises to 5 to 15° C. (41 to 59° F.) and later falls to 5 or 10° C. (41 to 50° F.). The cooling is then discontinued, and the temperature allowed to rise as high as 15 or 20° C. (59 to 68° F.). Cooling is again started and the product stirred until the temperature falls. The mixture is allowed to stand until all fibers disappear, and water is added to promote hydrolysis, as in the Miles process. With proper temperature control, this process is stated to yield a product of high viscosity, insoluble in chloroform but soluble in acetone, etc.

According to British Patent No. 139,232 (1918) to J. O. Zdanowich, a good grade of cellulose acetate suitable for the manufacture of acetate silk may be prepared by treating 150 grams of purified cellulose with a mixture of 500 cubic centimeters of glacial acetic acid and 420 cubic centimeters of acetic anhydride. While agitating, chlorine gas is passed into the mixture at 70 to 80° C. (158 to 176° F.). After two or three hours, 2 grams of sulfuric acid are added and stirring continued until a clear solution is obtained.

British Patent No. 258,020, June 17, 1925, to H. J. Mallabar states that cellulose acetate which is solüble in acetone, free from sulfuric acid residues, and does not char when heated, may be prepared by acetylating cellulose in the absence of sulfuric acid, but after a pretreatment with a mixture of acetic and sulfuric acids, the sulfuric acid being subsequently neutralized before the acetylation proper is effected. Zinc chloride is used as a catalyst during the acetylation. For example, 100 parts of cellulose are treated for 24 hours with a cold mixture of 400 parts of acetic acid and 2 to 5 parts of sulfuric acid, and then 200 parts of acetic acid, containing sufficient sodium acetate to convert the sulfuric acid into sodium sulfate, 15 to 25 parts of zinc chloride, and 250 to 400 parts of acetic anhydride are added, and the mixture is maintained at 30 to 40° C. until acetylation is complete. The resulting cellulose acetate may be precipitated directly from the product

and afterwards converted into an acetone soluble form by dissolving it in acetic acid, and maintaining the solution at 100° C.

Ost[4] states that some primary acetates show a partial but fugitive solubility in acetone; and while their films from chloroform are good, those from acetone are poor and can only be partially redissolved in acetone. On the other hand the acetone films from the secondary products are good, and complete solubility in acetone is a permanent characteristic. He also states that a "pure cellulose triacetate" may be obtained by treating 100 parts of cellulose, purified by treatment with dilute caustic soda and containing 5 to 6 per cent of moisture, with 400 to 500 parts of acetic anhydride, 400 to 500 parts of glacial acetic acid and 50 to 100 parts of fused zinc chloride. After about three weeks' time at 20° C. (68° F.), the triacetate is obtained, containing 62.5 per cent of acetic acid. At 10 or 12° C. (50 or 54° F.), several months' treatment are required to complete the reaction. Higher temperatures (60 to 70° C.) shorten the period of esterification but cause considerable breaking down of the cellulose molecule, and the resulting product is of little value. The triacetate formed at 20° C. (above) dissolves in pure chloroform but is more soluble in the presence of some alcohol, in which case viscous solutions may be obtained. As a primary acetate it is not soluble in acetone.

Barnett[5] prepared cellulose acetate from filter paper by pouring 200 grams of glacial acetic acid, containing just sufficient chlorine to color it, on 50 grams of the paper. After standing for some time, 250 grams of acetic anhydride were added, and a few bubbles of sulfur dioxide passed through the mixture. The temperature at once increased, and when maintained at 65° C. (149° F.) by cooling, a clear solution of cellulose diacetate (?) was obtained in about an hour. This product was soluble in chloroform, acetone, pyridine, aniline, hot nitrobenzene; and slightly soluble in a mixture of benzene and alcohol.

In another experiment, 5 grams of filter paper was immersed in 20 cubic centimeters of glacial acetic acid and 20 cubic centimeters of acetic anhydride containing 0.32 gram of chlorine added. Then 2 cubic centimeters of acetic anhydride containing 0.26 gram of sulfur dioxide were further added, whereby the mixture rapidly

gelatinised and solution was complete within 5 minutes. White flakes of cellulose triacetate were separated from the product.*

It is understood that at the present time, cellulose acetate is prepared[b] on a commercial scale in the Rhone district of France by treating the cellulose in large mixers with the acetic and sulfuric acids and 20 or 25 per cent of the acetic anhydride in small quantities at a time and then adding the balance of the acetic anhydride necessary to complete the reaction. The cellulose is quickly acted upon, soon losing its structure and dissolving to a clear solution. This chloroform soluble product is "ripened" by the action of water and heat until the desired properties are obtained, when the solution is further diluted with water to precipitate the cellulose acetate. On an average with various processes, 100 parts of cotton, 350 parts of glacial acetic acid, and 400 parts of acetic anhydride yield 150 parts of primary cellulose acetate. A large part of the acids are recovered from the process.

When cotton is immersed in a mixture of 50 parts of acetic anhydride, 50 parts of glacial acetic acid and 4 to 6 parts of sulfuric acid at 30 to 40° C. (86 to 104° F.), it rapidly dissolves to form

$$(C_6H_7O)_4SO_4(C_2H_3O_2)_{10}$$

Thus, as in the nitration of cellulose, the acetylation is incomplete in the presence of sulfuric acid. The acetic acid content in this case, if cleavage of the molecule is avoided, is only 59 to 61 per cent and sulfoacetate is formed simultaneously, the quantity depending upon the amount of sulfuric acid used as catalyst. Pure, high molecular acetates, free from sulfoacetates, cannot be prepared with sulfuric acid as catalyst. At a temperature of 10 to 15° C. (50 to 59° F.), two to four days acetylation in the presence of 5 or 10 per cent of sulfuric acid gives the best result. Prolonged acetylation at low temperatures appears to increase the amount of combined acetic acid in the product, with a consequent decrease in the amount of combined sulfuric acid. With increasing time and temperature, the sulfuric acid causes a greater acetoly-

*Also see U. S. Patent No. 1,600,159, September 14, 1926, to Zdanowich.

[b]Probably by a process similar to British Patent No. 237,567, July 28, 1924, to the Société Chimique des Usines du Rhone.

tic decomposition of the cellulose molecule. When only 1 or 2 per cent of acid is used the acetylation is complete in a few hours at 35 to 40° C. (95 to 104° F.)

When used as catalyst, acids combined with weak bases are far more moderate in their action on the product than sulfuric acid. For instance, when methylamine sulfate is used as catalyst, temperatures may be increased to 35 or even 50° C. With 5 to 10 per cent of methylamine sulfate at 35° C., several days are necessary for the complete acetylation; but the molecular cleavage is slight even in ten days. At 65 to 70° C. the danger is increased considerably, but the acetylation is complete in two hours. The composition of this methylamine sulfate cellulose acetate is similar to that obtained with sulfuric acid but it contains less sulfoacetate. According to Ost,[4] pure acetates of low acetic content are difficult to obtain as primary acetates. If insufficient acetic anhydride is present to form the triacetate, a portion of the cellulose remains unaltered while the composition of the acetate formed approaches that of the triacetate. Insufficient time or catalyst (zinc chloride) affects the final product in the same manner.

Unsaturated esters are readily obtained with either an excess or a deficiency of acetic anhydride, if a large proportion of sulfuric acid or methylamine sulfate is used. The acetic acid content of the final cellulose acetate may fall to 48.5 per cent (diacetate), and even below 40 per cent, but with a simultaneous rise of combined sulfuric acid of from 2.3 to 7 per cent. These mixed esters are partially hydrolyzed on precipitation with water; are increasingly insoluble in chloroform, in which they swell; but dissolve with increasing sulfuric acid content in alcohol and finally in water. While pure cellulose triacetate may be preserved for years and is not affected by boiling water, products containing sulfoacetates split off sulfuric acid on boiling in water.[c]

It is interesting to note here that Caille[6] found that acetate silk which contains combined sulfuric acid resists hydrolysis even on heating with water at 120° C. (248° F.), if the sulfuric acid groups have been neutralized by washing with calcerous water. Any unneutralized portion of such groups readily split off on heating the acetate silk with water.

[c] See page 36.

According to Ost,[4] only a portion of any primary cellulose acetate is extracted by pure acetone, this extraction being least in the case of a zinc chloride triacetate and most in the case of a methylamine sulfate product, often amounting to from 50 to 80 per cent of its weight. While the chloroform solubility is constant, the acetone solubility is not. An acetone film from a primary acetate made by the solution method is only partly soluble in acetone a second or third time. None of the true primary triacetate is soluble in acetone; but only secondary acetates which result from partial hydrolysis. Ten per cent of aqueous mineral acid at 20° C. or 1 per cent at 100° C. (212° F.) produces hydrolysis of the triacetate and may not give an acetone soluble product. Real and permanent acetone solubility is produced by partial hydrolysis of primary acetates of low acetic acid content and high sulfuric acid content, by stirring a little acid water into the finished acetylated syrup.[d]

Exceptional acetone solubility results upon heating a primary cellulose acetate or the primary syrup, after neutralization of the sulfuric acid, with ninety-five per cent acetic acid for sometime. Hydrolysis takes place in from twenty-four to ninety-six hours to a combined acetic acid content of from 56.2 to 50.8 per cent. Heating in the presence of small quantities of catalysts, such as sodium bisulfate, gives similar results. Heating with aniline or phenol, in the presence of a little water, also hydrolyzes it to the acetone-soluble form. Solubility in acetone is not connected with any definite degree of hydrolysis, the limits of the combined acetic acid varying between 57.6 and 50.9 per cent or even more widely.

Primary acetates prepared from previously hydrolyzed cellulose are very similar to those prepared from ordinay cellulose. The resulting films appear to be just as good, but generally the solutions are of lower viscosity and the precipitated products are more pulverulent. Hydrocellulose is more readily acetylated than ordinary cellulose, the reaction proceeding more rapidly with a smaller quantity of catalyst and at a lower temperature. Secondary acetates are produced from these products in the same manner as from those prepared from normal cellulose.

[d] See German Patent No. 252,706.

*"Catalysts"*

While the sulfuric acid used in acetylating cellulose is usually spoken of as a catalyst or as a condensing agent, its function appears to be almost entirely due to its degradating action upon the cellulose, with the consequent formation of hydrocellulose. Various workers have shown that the acetylation of hydrocellulose is much more rapid than that of cellulose. It is therefore possible that, as the mineral acid acts upon the cellulose to form hydrocellulose, this product is immediately broken down to form the cellulose acetate.

Heuser[7] in discussing the role of catalysts in the acetylation process, divides the action of sulfuric acid, either free or combined, into four stages:

1. Hydrolysis of the cellulose to cellulose dextrin.
2. Esterification of the cellulose dextrin with sulfuric acid to sulfuric acid esters of cellulose dextrin.
3. Esterification of the sulfuric acid esters by means of acetic anhydride, forming sulfoacetates.
4. Splitting off of the sulfate residues; that is, the establishment of a definite ratio between sulfate and acetate residues, dependent upon the conditions of the experiment.

He also points out the hydrolysis of zinc chloride in solution, and says that it is very evident from the quantity of these materials required in the acetylation process that their role is not strictly that of a catalyst. While they do start and accelerate the reaction, their part is, possibly, principally that of a peptizing agent, rather than that of a catalyst. These catalysts no doubt act on the cellulose in such a manner as to render it more reactive with the acetic anhydride; and while in most instances their action on the cellulose is not great, the resulting acetate is not a pure cellulose acetate, when they are used. Acetic acid acts as a solvent for the reaction as well as the acetate formed; but alone, it has very little esterifying action on cellulose even at high temperatures.

Barnett,[5] in discussing the catalysts, says that most of them are strong dehydrating agents and as examples mentions sulfuric acid,

phosphoric acid, zinc chloride, chlorides and oxychlorides of sulfur and phosphorous, dimethylsulfate, chloroacetic acid, etc. Chlorine does not react readily except under special conditions and then only slowly. Sulfuric acid tends to give dark colored solutions and to hydrolize the product. It may also cause brittleness in the resulting film, due to its incomplete removal. Sulfuryl chloride[e] is claimed to give a superior product. Either chlorine or sulfur dioxide alone give poor results as catalysts; but when traces of both are introduced either separately or together, the acetylation proceeds to a remarkable extent, giving a prefectly clear solution or jelly.[f] This catalyst is also useful in the preparation of other cellulose esters, such as the butyrate, benzoate (using benzoyl chloride in acetic acid), etc. He attributes the great reactivity of this mixed catalyst to a possible condensation of the chlorine and sulfur dioxide upon the cellulose itself, which produces a small amount of sulfuryl chloride *in statu nascendi* in intimate contact with the cellulose. The reaction proceeds best when the amounts of chlorine and sulfur dioxide are approximately in the ratio of their molecular weights.

Levy in a recent patent[g] proposes the use of some new catalytic agents in connection with the preparation of cellulose acetate. He states that acetone soluble cellulose acetate may be rapidly prepared by treating air-dry cellulose, which contains 6 to 7 per cent of moisture, with a mixture containing acetic acid, acetic anhydride, a condensing agent such as sulfuric acid, and a catalyst such as the acetate or sulfate of vanadium, nickel, cobalt, or chromium. The metallic salt apparently has the function of a true catalyst, the metal being the active element, and therefore it may be introduced in the metallic form, passing gradually into solution as the reaction proceeds.

For example: 25 pounds of cellulose are kneaded at a temperature not exceeding 15° C. in a mixture containing 5 pounds of acetic acid, 5 pounds of acetic anhydride, 0.2 pound of sulfuric acid and 2.5 grams of chromium acetate, until a transparent, viscous liquid, free from fibers is obtained. This mixture is then

[e] See British Patent No. 24,382 of 1910.
[f] Also see British Patent No. 139,232.
[g] L. A. Levy, British Patent No. 240,624, April 9, 1924.

held at 30° C. until the resulting cellulose acetate is freely soluble in acetone. The preparation is complete in 18 hours or less. Salts of magnesium, aluminum, sodium, antimony, uranium, manganese, cerium, tin, niobium and thorium are not suitable catalysts.

### *Stability*

Caille[6] has shown that the stability of cellulose acetate in the presence of hot water is very considerably increased by the presence of sulfuric acid groups which have been neutralized by means of calcerous water (lime). If these sulfuric acid groups are not neutralized in this manner, but remain combined with the cellulose ester or free, the resulting technical cellulose acetate is more or less unstable and subject to decomposition, the extent depending upon the amount of mineral acid present in the product. It has recently been shown that the sulfuric acid groups present in cellulose ester silk (acetate or nitro) greatly influence its dyeing properties. Entat and Vulquin[11] state that the amount of sulfuric acid present as sulfoacetic acid in technical cellulose acetates of good grade does not exceed 0.03 per cent, but that in every case where sulfuric acid or its derivatives are used as catalysts, the resulting product contains some mineral acid combined as a sulfoacetic acid ester of cellulose.

They state that the free sulfuric acid may be estimated by digesting a 10 gram sample with 200 cubic centimeters of water at 15° C. for 30 minutes, filtering and titrating the filtrate electrometrically with standardized barium hydroxide solution. The electrometric titration curve shows a sharp break when the free sulfuric acid is neutralized. They determine the sulfoacetates present by heating a 5 gram sample with 50 cubic centimeters of water for 5 hours at 125° C. in an autoclave. The sulfuric acid resulting from the hydrolysis of the sulfoacetate is then titrated as above.

### *Solubility of Cellulose Acetate and Acetate Silk*

A. Eichengruen has pointed out that a whole series of cellulose acetates, many of them more or less indistinguishable from each other analytically, are possible and exist in some cases. There are

many reasons for this variation in composition, as we have seen in the discussion of their manufacture, etc. Probably the greatest analytical differences are apparent in the mono-, di-, and triacetates, yet many others are possible. Our two best known acetate silks, Celanese and Lustron, differ considerably in their acetate content, the Lustron containing a considerably larger proportion of acetate groups than Celanese. In the case of cellulose nitrate, it has long been known that its alcohol-ether solubility is not a function of the nitrogen content alone. In the case of the cellulose acetates, probably even a wider discrepancy exists between the total acetate content and the solubility in any one solvent or solvent mixture. For this reason it is rather difficult to specify the solubility of cellulose acetate in any solvent or mixture of solvents with diluents or other compounds.

One of the factors, which complicates this matter, is that of hydrolysis after the acetylation. The primary cellulose triacetate is soluble in chloroform, while the partially hydrolyzed secondary product is less soluble in chloroform but more soluble in acetone, depending upon the extent of the hydrolysis. The constitution of these partially hydrated or hydrolyzed cellulose acetates varies gradually from complete solubility in chloroform to incipient plasticity in cold or warm chloroform, with a parallel increasing solubility in anhydrous acetone.

Carried beyond this point, the hydrolysis results in products of less value, but greater solubility in mixtures of acetone and water, until eventually products soluble in benzene, benzine, and finally in water alone, result. Worden[8] states that coincident with hydration is the loss of acetic acid, but the stages are indistinguishable, and the solubility results are not always dependent upon the acetic acid content. Hydrolysis of the cellulose aggregate in the ester appears to take place coincident with elimination of acetic acid, so that two variables are simultaneously introduced. For this reason the majority of the solubility determinations found in the technical literature are practically worthless for systematic generalizations, because the nature of the normal (primary) or hydrated (secondary) cellulose acetate used in the experiments

is not stated, or the conditions under which the determinations were made are not recorded.

Hess[9] attributes the variable solubilities of cellulose triacetate in its different forms as due to the influence of small quantities of impurities. The triacetates which are soluble in chloroform or tetrachlorethane show a specific rotation with sodium light of approximately —20° in these solvents and —50° in pyridine. They can be produced in the form of large crystals from solutions in tetrachlorethane or in ethylene-tetrachloride. Presumably these acetates form molecular combinations with the solvents. The lower acetates, soluble in acetone, show a specific rotation, with the same light, of only about —21° in pyridine. He also states that the ideas of polymerisation and depolymerisation of the cellulose molecule are untenable, and that it reacts as a chemical unit $C_6H_{10}O_5$, rather than as $C_{12}H_{20}O_{10}$. Herzog and Kruger[10] report that their experiments indicate that cellulose acetate disperses in acetone when the diameter of the particles is less than 20 *uu*, in ethyl acetate when less than 5 $\mu\mu$, and in epichlorohydrin when less than 35 $\mu\mu$.

The following is a list of some of the most common chemicals which have considerable solvent power for some or all of the cellulose acetates. No attempt will be made to enumerate the non-solvents, for in many cases, in the presence of other compounds, usually cellulose acetate solvents, some of the so-called non-solvents aid materially in the solution of the acetate. The compounds enumerated below should never be present in scouring baths or dry-cleaning solvents for use upon materials containing acetate silk.

Chloroform, acetone, tetrachlorethane, alcohol of various strengths, phenol, cresols, light acetone oil, acetic acid, nitrobenzene, pyridine, aniline, triacetin, toluidine, xylidine, mono-, di-, and epi-chlorhydrin, acetylene tetrachlorde and ethyl acetate, benzyl alcohol, diacetone alcohol, cyclohexanone and other cyclic ketones of the same series, etc.[h]

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[h] Also see Chapter V on Identification of Rayons, and Worden, "Technology of Cellulose Esters." Vol. VIII.

*Manufacture of Acetate Silk*

As to the actual conversion of the cellulose acetate into acetate silk, very little outside of the patent literature has been published. Without doubt the cellulose acetate is thoroughly washed until free of acid, the sulfuric acid neutralized, and the ester dissolved in a suitable solvent, for spinning. Very possibly, in the case of Lustron,[1] this solvent solution contains tetrachlorethane. In the manufacture of Celanese, probably a more volatile solvent is used, such as acetone, perhaps in combination with other solvents or diluents.

The formation of the acetate silk fiber from these solvent solutions differs very considerably in that with Lustron, and probably some other products, the fiber is formed by spinning the solution into a suitable precipitating bath; while in the case of Celanese, and possibly in that of all related companies, the "dry spinning" process is used, wherein the fiber is formed not by precipitation, but by the evaporation of the solvent in a current of warm air. From the information available and patents[1] which have been granted to the manufacturers, it would appear that Rhodiaseta is manufactured by the dry spinning process, probably in a manner more closely resembling the Celanese process than that of Lustron.

United States Patent No. 1,551,112, August 22, 1923, to H. S. Mork and C. F. Coffin, Jr., assignors to the Lustron Company, covers the use of a solvent solution containing tetrachlorethane and an aliphatic hydrocarbon for the cellulose acetate, and this is spun into a coagulating bath containing an aliphatic hydrocarbon.

British Patent No. 165,519, March 26, 1920, to the British Cellulose and Chemical Manufacturing (Parent) Company and H. B. Roy, covers the production of artificial threads and filaments by spinning solutions of cellulose acetate, or other cellulose derivatives in volatile solvents, downwards through a hollow casing in a current of warm air, to remove the solvent. The finished thread is passed through a small hole in the side of the casing and wound by suitable apparatus. A travel of 2 or 3 seconds in a current

[1] See United States Patent No. 1,583,475.

of air at 30 to 50° C. (86 to 122° F.) removes the solvent efficiently.

British Patent No. 248,696, May 27, 1925, to G. B. Ellis, from the Soc. Fabr. de la Soie "Rhodiaseta," states that in dry spinning solutions of cellulose derivatives in volatile solvents, the cross-section of the filaments may be controlled, so as to avoid flat scintillating effects and obtain the rounder or star-shaped type, by ensuring at the spinning apertures an imput of heat, maintaining at the spinning dies and in the immediate neighborhood a temperature regulated and varied according to the demand of the other spinning conditions, independently of the temperature of the cell.

United States Patent No. 1,583,475, May 4, 1926, to J. E. G. Lahousse, assignor to the Soc. Fabr. de la Soie "Rhodiaseta," and British Patent No. 238,842, cover the preparation of acetate silk fibers from a solution of cellulose acetate in a volatile solvent by the dry spinning process. The evaporating medium, previously richly laden with a definite proportion of the vapors of the solvent but not saturated at the temperature of the cell, is introduced into the closed cell so as to control the speed of drying of the fiber. In this way they claim to be able to control the cross-section of the filaments.

*Fibers of Mixed Cellulose Esters*

From time to time numerous patents have been granted for rayon fibers consisting of more than one variety of cellulose ester, or other mixture of cellulose compounds. While these patents represent an interesting possibility, if these fibers are now prepared on a commercial scale, they have not as yet found any considerable use in America. However, they may eventually appear upon the market. The following patents serve as examples of the proposed fibers:

British Patent No. 11,625, May 17, 1909; French Patent No. 402,072, April 15, 1909; German Patent No. 240,751, July 4, 1908, and No. 248,559 (1909) to L. Lederer cover the production of fibers of a mixed constitution containing cellulose acetate. For instance, a spinning solution containing 5 or 6 parts of cellulose trinitrate, to 2 parts of triacetate, in 27 parts of acetone

and 16 parts of acetylene tetrachloride is suggested. Precipitation is effected by alcohol. The resulting fiber may be denitrated, and it is claimed that the resulting thread has a good strength even in the moist condition and may easily be dyed.

British Patent No. 211,889, February 23, 1924, to W. J. Mellersh-Jackson, for the Tubize Artificial Silk Company of America, covers the production of clear lustrous rayon threads or like products by spinning solutions of cellulose nitrate in admixture with organic acid esters of cellulose; for instance, cellulose acetate, in acetone or its homologues, or mixtures thereof, with other solvents such as ethyl alcohol. The solvent is extracted from the filament by the action of a concentrated aqueous solution of calcium chloride, which has no effect on the cellulose esters and is miscible with acetone. The solvent is of course recovered from the calcium chloride solution. The threads produced by this process are denitrated in the usual manner.

### *Manufacture of Colored Acetate Silk*

As a result of the early difficulties in dyeing acetate silk, not all the research was directed towards the production of new and special methods of dyeing, and dyes for, this new fiber. Another phase of this research led to certain processes and patents for the manufacture of a colored artificial silk.

One of the first processes along this line was British Patent No. 1556 of 1911, to F. Bayer and Company, also covered by French Patent No. 427,445, March 16, 1911; German Patent No. 237,210 of 1910; Austrian application A2376-11, March 16, 1911; Belgium Patent No. 233,786 of 1911; and United States Patent No. 994,738, June 13, 1911, to E. Friedman. According to this process, the cellulose is dyed before acetylation with dyestuffs capable of withstanding acid treatment and then acetylated in the usual manner. Suitable dyes mentioned are Algol Red, Helindone Scarlet, Rosanthrene, Diazo Brilliant, Scarlet, Algol Blue, Indanthrene Blue, Katigen Brilliant Green, Katigen Violet, Diazo Indigo Blue, Katigen Black or Immedial Black. In the case of Katigen Brilliant Green G, a sulfur dyestuff, 10 per cent on the weight of

the goods is suggested, and it is claimed that in most instances the color is even purer in the acetate silk than on cotton.

W. G. Lindsey, assignor to the Celluloid Company, in United States Patents No. 1,041,115-6-7 and 8, October 15, 1912, mentions that acetyl-cellulose, soluble in acetone, may be mixed with camphor, triphenyl or tricresyl phosphate, methyl or ethyl alcohol, etc., and coloring matters or other inert substances.

According to United States Patent No. 1,041,587 (October 15), British Patent No. 12,995 (June 3, 1912), Belgium Patent No. 246,562 (1912), D. R. Anm. B-63, 482 (1911), and French Patent No. 444,588, to B. Borzykowski, a colored acetate silk may be manufactured by dissolving the dyestuff, such as Bismark Brown, Chrysophenine G, Fast Scarlets, substantive blacks, etc., directly in the acetylating bath, before the introduction of the cellulose. When the cellulose acetate is precipitated for purification the dyestuff remains in the acetate, giving a bright and clearly dyed product. Resolution of the cellulose acetate in cholorform, acetone, or dichlorethylene gives a clear solution without alteration in shade.

British Patents No. 226,309, October 10, and No. 227,146, October 19, 1923, to L. A. Levy, propose to color the acetate silk by adding suitable dyes to the acetone solution of the cellulose acetate, before dry spinning (Celanese process).

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[3] M. Deschiens, *Chemistry and Industry 44*, 902-7 (1925).
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[6] A. Caille, *Chim. et Ind. 13*, 11-13 (1925).
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[12] F. Sproxton, "Cellulose Ester Varnishes," 1925.
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# CHAPTER IV

## THE GENERAL PROPERTIES OF ACETATE SILK (EXCEPT DYEING PROPERTIES)

*Its Resistance to Water, Acids, Alkalies, and Micro-Organisms. The Relation of Regain to Strength and Elasticity. Electrical Properties, Flammability, Luster, Specific Gravity, Refractive Index, and Structure.*

FROM our present knowledge of the constitution of acetate silk, we would expect it to have somewhat different properties from those of the older rayons, none of which approach it in chemical composition; and many of these properties of acetate silk are highly desirable in a textile fiber. In fact in some respects this product more closely resembles true silk than any other known fiber. It has a high luster; good tensile strength which it retains to a greater extent than the other rayons when wet; a high elasticity, especially in the case of Celanese; a soft, full, silky feel in the fabric; an extremely high resistance to micro-biological injury such as mildew, mold, and bacteria; a high thermal and electrical insulating value; a low flammability; low specific gravity; etc. Its dyeing properties are also especially interesting, but we will not attempt to discuss them in the present chapter.

### *Water Resistance and Wetting-Out*

Acetate silk does not swell appreciably in either hot or cold pure water nor in absolute alcohol, but swells in mixtures of water with alcohol or many other organic solvents. It has a high resistance to wetting-out with pure water, and its strength when wet is proportionately greater than that of the other rayons, as shown in the various tables which follow. Cold water alone has little detrimental action on the fiber even when in contact for long periods of time. The resistance to hot water varies with the product. In the case of Celanese and Rhodiaseta, boiling water destroys the luster, therefore it should not be wet-processed (scoured or dyed)

at over 82° C. (180° F.). On the other hand, Lustron will withstand boiling water for sometime without ill effects.

In fact, the older or original acetate silks (primary cellulose triacetates) were so hard to wet-out with aqueous solutions that it

*a* *b* *c* *d* *e* *f*

FIGURE I

Showing Viscose (*a*), Du Pont (*b*), Industrial Fiber (*c*), Lustron (*d*), Celanese (*e*), and Cuprammonium (*f*) Silks

*Courtesy Associated Knit Underwear Manufacturers of America*

was almost impossible to wet them out completely and evenly in a practical way with aqueous solutions of the ordinary dyeing materials. Apparently, as might be expected, the present-day hydrolyzed or secondary cellulose acetate silks are much easier to wet-out than

the older products. Of our present acetate silks, Lustron which approaches a triacetate in composition, is no more difficult to wet-out than Celanese, which more nearly corresponds to a cellulose diacetate. This may be due to some special treatment during its manufacture, or to some finishing process. Again it is possible that in the case of Lustron, the addition of suitable compounds to the spinning or precipitating solutions may aid in wetting-out the finished product.

For instance, United States Patents No. 712,200 (1902), and No. 792,149, June 13, 1905, to A. D. Little, H. S. Mork, and W. H. Walker, cover the addition of compounds such as oleic acid, phenol, cresols, etc., to the cellulose acetate in order to render the acetate silk more pliable. It is well known that the three compounds mentioned above considerably lower the surface tension of aqueous soap solutions, and it is very possible that they play an important part in wetting-out Lustron.

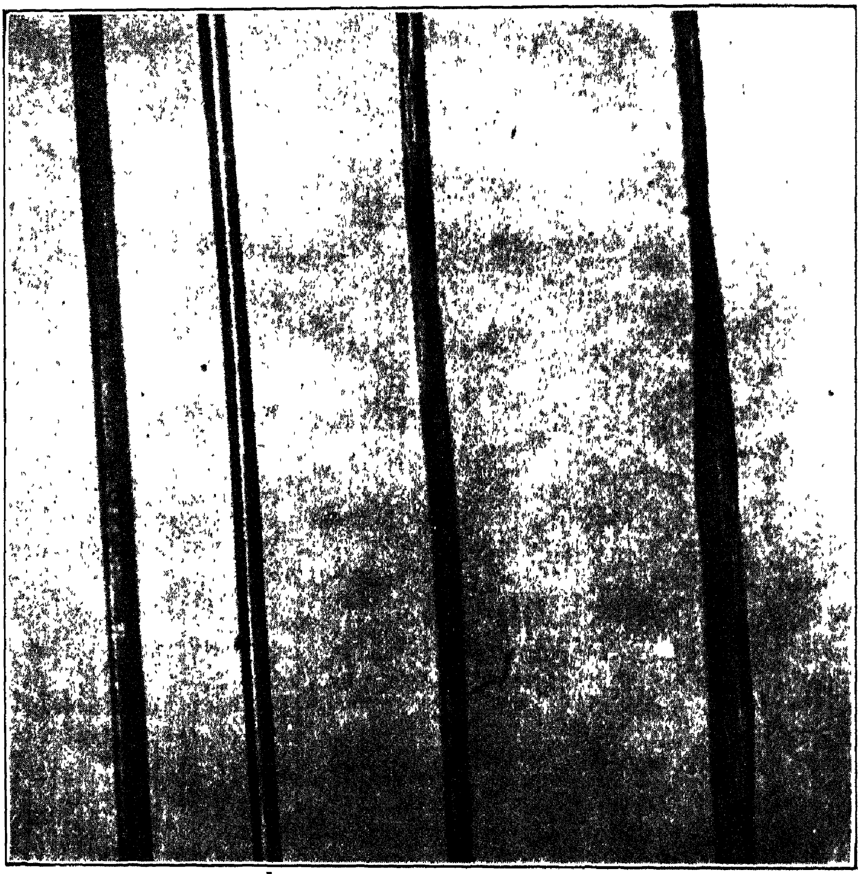
### *Regain*

Acetate silk normally has the lowest regain of any commercial textile fiber and does not take up the moisture or water to the same extent as the other textile fibers, including the older rayons. The low permeability of acetate silk to water and aqueous solutions has been explained as due to its low porosity, and for this reason it is common to use more concentrated aqueous solutions in treating it; as, for instance, in diazotizing and developing, than for the other fibers.

One of the principal difficulties with the other rayons has been their low tensile strength when wet. It was at one time even difficult to piece-dye some of the rayons without damaging the fabric. However, in most instances this difficulty has been overcome to a large extent, but they are still not all that could be desired in this respect. A number of methods for waterproofing or lowering the water absorption of the older rayons have been proposed, in order to improve their wet strength. The "sthenose"[a] process appears to have received the most publicity and has been stated to consist of a formaldehyde and lactic acid treatment of the yarn. While

[a]See British Patent No. 25, 647 of 1906.

the rayon is waterproof, it becomes more harsh and its dyeing properties are altered, as would be expected. Dr. Luft proposed a process based upon treating viscose rayon with aluminum acetate during the desulfurization. Very probably this treatment would also considerably alter its dyeing properties.



a b c d

FIGURE II

Showing Viscose (*a*), Celanese (*b*), Cuprammonium (*c*), and Tubize (*d*), Silk Fibers

*Courtesy Associated Knit Underwear Manufacturers of America*

Another idea along the same line is covered by British Patent No. 253,854, July 17, 1925, to L. Lilienfeld, which states that the tensile strength of viscose, cuprammonium, Chardonnet and acetate silks may be increased from 40 to 100 per cent by impregnat-

ing the yarn in skeins or fabric with a solution of cellulose thiourethane in which at least one hydrogen atom of the amino group is replaced by an alkyl radical, the solvent being subsequently removed. Suitable solvents include aqueous solutions of alkalies such as sodium hydroxide or ammonia, which of course would be unsuited for use on acetate silk, and volatile solvents such as pyridine. The rayon is preferably stretched during the treatment, as specified in British Patent No. 253,853, and the impregnated silk may be rendered highly flexible by exposure to the vapors of a suitable organic solvent, such as pyridine, as described in British Patent No. 231,806 and No. 248,994.

### *Regain and Strength*

Normally, acetate silk contains less than 5 per cent of moisture (condition), and even when wet, it retains only about a third or a half as much water as the other rayons. This apparently accounts for its superior strength, as compared with the other rayons, when wet. Palmer[1] writes that whereas the older rayons retain about one third of their strength when wet, acetate silk is two thirds as strong wet as dry. When the acetate silk contains the same amount of water as the older rayons, it does not appear to be any stronger than the others. However, due to its low porosity and permeability, acetate takes up water rather slowly and to a smaller extent than the other rayons under the same conditions and therefore retains a larger proportion of its dry strength, when wet, than the other rayons.[b]

WET AND DRY STRENGTHS OF VARIOUS RAYONS

| *Variety* | *Titer* | *Dry Strength* | *Absolute Wet Strength* | *Relative Wet Strength* |
|---|---|---|---|---|
| Glanzstoff | 147.5 | 1.45 | 0.58 | 39.87 |
| Agfa | 184.5 | 1.27 | 0.56 | 44.3 |
| Spinnerfaser A.G. | 182. | 1.47 | 0.66 | 44.9 |
| Acetatseide | 134. | 0.88 | 0.43 | 48.9 |

[b] Suchanck[30] states that if the wet and dry strength of acetate silk is compared with that of the other rayons on the basis of the relative loss of strength, or of the percentage loss of strength calculated on its dry strength, the supposed superiority of wet acetate silk over the other wet rayons is very slight. He gives the above table showing these figures, but does not state what variety of acetate silk was used in making the tests. Probably it was one of the Continental products.

Prof. Grimshaw[2] reports experiments which show that when Celanese is exposed to an atmospheric relative humidity of 84 per cent, the equilibrium regain is only 8.59 per cent; while under the same conditions cotton has 12.5 per cent of regain and viscose

FIGURE III
True Silk Fibers
*Courtesy Associated Knit Underwear Manufacturers of America*

15.69 per cent. Under room conditions, wherein cotton had 6.8 per cent of regain and viscose 9.52 per cent, Celanese had only 3.57 per cent of regain. In other words it usually contains only about one-third to one-half as much moisture as the other rayons.

Parker and Jackman[3] report that after drying the various textile fibers for five days over phosphoric acid at 21° C. (70° F.), they

contained the following amounts of moisture: Celanese, 0.1 per cent; viscose, 2.2 per cent; cotton, 0.8 per cent; linen, 1.0 per cent; normal and chlorinated wool, 2.0 per cent; silk 1.1 per cent. Celanese does not appear to reach equilibrium with the atmosphere, from the dry condition, as rapidly as cotton, but more quickly than wool, silk, or viscose.

Prof. Johnson[4] investigated the relative hygroscopic properties of the different rayons at various relative humidities. His results are shown in Table V. It is interesting to note that at low humidities, Lustron appears to be more hygroscopic than Celanese, in the ratio of 1.0 to 0.89; while at higher humidities, Celanese is more hygroscopic, in the ratio of 1.17 to 1.0.

TABLE V

AVERAGE RESULTS OF TESTS UPON THE REGAIN OF RAYONS AT 15 PER CENT (A), 68 TO 61 PER CENT (B), AND 76 TO 61 PER CENT (C), RELATIVE HUMIDITIES

| | *A (75° F.)* | *B (70° F.)* | *C (72° F.)* |
|---|---|---|---|
| Nitro (Tubize), 150 denier | 6.79 | 15.4 | 16.6 |
| Viscose, 300 denier | 6.60 | 14.4 | 15.5 |
| Cuprammonium, 120 denier | 7.18 | 14.6 | 16. |
| Celanese, 150 denier | 1.91 | 6.87 | 7.74 |
| Lustron, 300 denier | 2.15 | 5.49 | 6.61 |
| Mercerized cotton | —— | —— | 8.24 |

Hassac[31] investigated the properties of six rayons in use about 1900 and his results are given in Tables VI and XIX. The first three samples are nitro silk, *a* from Pris de Vaux, near Besancon; *b* from Fisme in Northern France; and *c* from Watson, England. Sample *d* is a collodion silk made by the Lehner process at Glattburgg, near Zurich; *e* a cuprammonium silk prepared by Pauly's

TABLE NO. VI

PROPERTIES OF EARLY ARTIFICIAL SILKS, ABOUT 1900

| | *Moisture per cent* | | *Number of Fibers per 1 sq. mm.* | | *Tensile Strength* | | *Extension* |
|---|---|---|---|---|---|---|---|
| *Variety* | *Air-dry* | *Saturated* | *Wet* | *Dry* | *Wet* | *Dry* | *Per Cent* |
| True Silk | 8.71 | 20.11 | 9,710 | 9,710 | 37.0 | 37.0 | 21.6 |
| (*a*) Pris de Vaux | 11.11 | 27.46 | 640 | 1,135 | 2.2 | 12.0 | 8.0 |
| (*b*) Fismes | 10.92 | 27.12 | 370 | 656 | 1.6 | 7.8 | 11.6 |
| (*c*) Walston | 11.32 | 28.94 | 683 | 1620 | 1.0 | 22.3 | 7.9 |
| (*c*) Lehner | 10.45 | 26.45 | 413 | 1180 | 1.5 | 16.9 | 7.5 |
| (*e*) Cuprammonium | 9.20 | 23 08 | 742 | 1550 | 3.2 | 19.1 | 12.5 |
| (*f*) Gelatin | 13.98 | 45.56 | 265 | 945 | Nil | 6.6 | 3.8 |

process at Oberbruch, near Aachen; and *f* is a sample of Hummel's gelatin silk.

Parker and Jackman[3] investigated the strength of different materials by means of the Mullen bursting test. Wool, true silk,

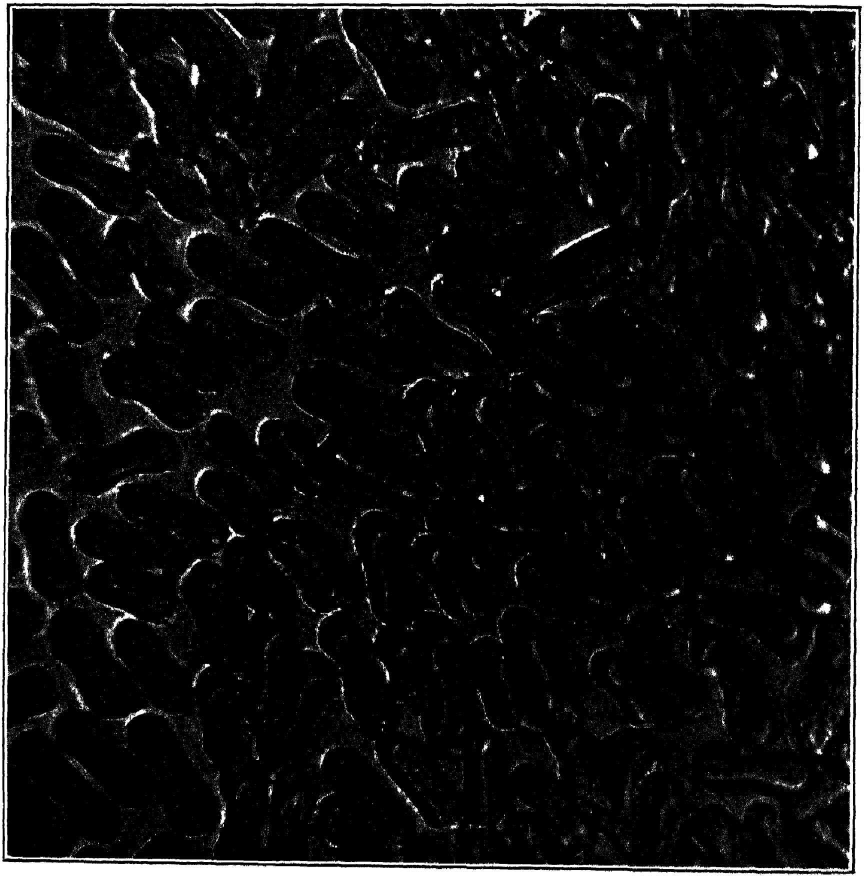


FIGURE IV
Cross-section of Lustron
*Courtesy Associated Knit Underwear Manufacturers of America*

viscose, and Celanese fabrics, both woven and knitted, showed a large and fairly regular fall in strength as the humidity increased, although when wetted, the loss with true silk was only half the loss with viscose, which was affected most. Celanese and wool showed

losses intermediate between those of true silk and viscose. Cotton and mercerized cotton showed a slight increase in bursting strength with rising humidity, while linen was 25 per cent stronger wet than when dry. In all cases the change in strength on wetting appears to take place rapidly. Pieces tested immediately after wetting and those tested after soaking for two days gave the same strength. The strength changes are only temporary, all fabrics reverting approximately to their original strength when reconditioned at, say, 70 per cent relative humidity.

Table VII gives a summary of their results.

TABLE VII

BURSTING STRENGTH OF FABRICS (MULLEN TESTER) UNDER VARIOUS CONDITIONS[3]

| *Treatment* | *Wool Woven* | | *Silk Knitted* | | *Jap Silk* | | *Celanese Knitted* | | *Celanese Woven* | | *Viscose* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % |
| Conditioned at 70% R.H. and 21° C. | 38 | 100 | 87 | 100 | 77 | 100 | 51 | 100 | 66 | 100 | 41 | 100 |
| Wet | 21 | 55 | 57 | 65 | 71 | 92 | 28 | 55 | 37.5 | 57 | 15 | 37 |
| Wet and hot, after boiling 1 hr. in distilled water | 19 | 50 | 49 | 56 | 55 | 72 | 24 | 47 | 30 | 45 | 15 | 37 |
| Wet, after 45 hrs. in 0.3% sodium oleate at 15°C. | 21 | 55 | 50 | 69 | 69 | 90 | 28 | 55 | 36 | 55 | 15 | 37 |
| Wet and hot, after 1 hr. in 1.0% sodium oleate at 60°C. | 18 | 47 | —— | | 61 | 79 | 28 | 55 | 38 | 58 | 15 | 37 |
| Wet and hot, after 1 hr. in 1.0% sodium oleate, boiling | 10 | 26 | —— | | 56 | 73 | 24 | 47 | 29 | 44 | 15 | 37 |
| Wet and hot, after 1 hr. in 1.0% sodium oleate, boiling | 13.5 | 35 | —— | | 57.5 | 75 | 29 | 57 | 35 | 53 | 16 | 39 |

TABLE VIII

STRENGTH OF 150 DENIER DU PONT VISCOSE AND CELANESE RAYONS IN 120 YARD LENGTH SKEINS ON A SCOTT TESTER[2]

| Moisture corresponding to a Cotton Regain of | *Break per Skein in Pounds* | |
|---|---|---|
| | *Du Pont Viscose* | *Celanese* |
| 6.7 per cent | 59.3 | 58.7 |
| 7.7 per cent | 60.0 | 61.0 |
| 12.5 per cent | 55.3 | 49.3 |
| 13.7 per cent | 55.0 | 49.7 |

## TABLE IX

COMPARATIVE STRENGTH OF VARIOUS RAYONS[6]

| | Tensile Strength Dry | Tensile Strength Wet | Extension |
|---|---|---|---|
| Chardonnet | 0.75 to 1.4 | 0.25 to 0.6 | 7.5 to 16.0% |
| Cuprammonium | 1.0 to 1.35 | 0.35 to 0.55 | 14.0 to 18.0% |
| Acetate | 1.1 | 0.7 | 18.0% |
| Viscose | 1.2 to 1.6 | 0.45 to 0.7 | 11.0 to 22.0% |
| Natural silk | 2.5 | 2.0 | 21.0 |

## TABLE X

MOISTURE IN DIFFERENT VARIETIES OF RAYON[7]

| Temperature °C. | Temperature °F. | Relative Humidity Per Cent | Raw Silk Per Cent of Moisture | Nitro Rayon, Process A Per Cent of Moisture (110 denier) | Nitro Rayon, Process B Per Cent of Moisture (110 denier) | Acetate Rayon, (Celanese) Per Cent of Moisture (175 denier) |
|---|---|---|---|---|---|---|
| 14.5 | 58 | 62 | 9.834 | 10.150 | 10.346 | 5.134 |
| 14.5 | 58 | 72 | 10.647 | 10.729 | 10.862 | 5.626 |
| 20.0 | 68 | 60 | 9.460 | 9.956 | 9.457 | 4.600 |
| 18.0 | 64 | 65 | 9.834 | 10.248 | 9.773 | 4.921 |
| 19.0 | 66 | 65 | 7.148 | 10.334 | 9.825 | 4.957 |
| 18.5 | 65 | 72 | 8.139 | 11.016 | 10.605 | 5.556 |
| 18.5 | 65 | 72 | 8.626 | 11.158 | 10.708 | 5.591 |
| 20.5 | 69 | 70 | 8.809 | 11.068 | 10.708 | 5.486 |
| 19.0 | 66 | 73 | 8.931 | 11.347 | 10.913 | 5.696 |
| 20.0 | 68 | 75 | 9.007 | 11.536 | 11.117 | 5.905 |

## TABLE XI

WET STRENGTH OF WET FIBERS, AS A PERCENTAGE OF THEIR DRY STRENGTH[8]

| | |
|---|---|
| Cotton | 110-120 per cent |
| Wool | 80- 90 per cent |
| Silk (true) | 75- 85 per cent |
| Acetate silk | 65- 70 per cent |
| Cuprammonium silk | 50- 60 per cent |
| Viscose silk | 45- 55 per cent |
| Nitro silk | 30- 40 per cent |

TABLE XII

ABSOLUTE RESISTANCE IN KILOGRAMS PER SQUARE METER OF VARIOUS FIBERS AND RAYONS[9]

| | *Dry Thread* | *Wet Thread* |
|---|---|---|
| Raw true silk | 50.0 | 41.0 |
| Weighted true silk | 20.0 | 15.0 |
| Collodion silk | 17.0 | 4.3 |
| Cuprammonium silk | 19.1 | 3.5 |
| Viscose silk | 21.5 | 3.5 |
| Cotton | 11.5 | 18.6 |
| *Diameters of Various Fibers* | | |
| Wool | 0.0005 to 0.002 inch | |
| Cotton | 0.0004 to 0.001 inch | |
| Silk about | 0.0007 inch | |
| Rayon about | 0.0018 inch | |

TABLE XIII

STRENGTH AND ELASTICITY OF EARLY RAYONS (ABOUT 1900)

(*On Basis of a Standard 100 Denier Thread*)

| *Type* | *Breaking Weight* | *Elasticity Per Cent* |
|---|---|---|
| Nitro by Chardonnet process (undenitrated) | 150 | 23 |
| Same, after denitrating and drying | 110 | 8 |
| Same, after denitrating but undried | 25 | — |
| Nitro by Bronnert process (undenitrated) | 125 | 28 |
| Same, after denitrating and drying | 115 | 13 |
| Same, after denitrating but undried | 32 | — |
| Natural silk | 300 | 18 |

TABLE XIV

PROPERTIES OF RHODIASETA BRAND ACETATE SILK, 75 DENIER YARN, 200 TURNS PER METER

| | *Dry* | *Wet* |
|---|---|---|
| Tensile strength in gr. per denier | 1.25 to 1.35 | 0.72 |
| Elongation in per cent | 23 to 25 | 35 |
| Real elasticity, per cent | 2.6 | |

It has recently been reported[32] that after immersion in water and squeezing under comparable conditions, fully saponified acetate silk retained 74 per cent of water, while the partially saponified fiber, such as that used in printing, retained only 50 per cent, and the unsaponified acetate silk (variety not stated) only 35 per cent of water.

*Elasticity*

Dr. Luft[9] states that there is a rather constant ratio between tenacity and elongation in relation to the moisture content of rayon. Rayon (except acetate) loses strength when wet because it readily absorbs about three parts of water to one part of dry

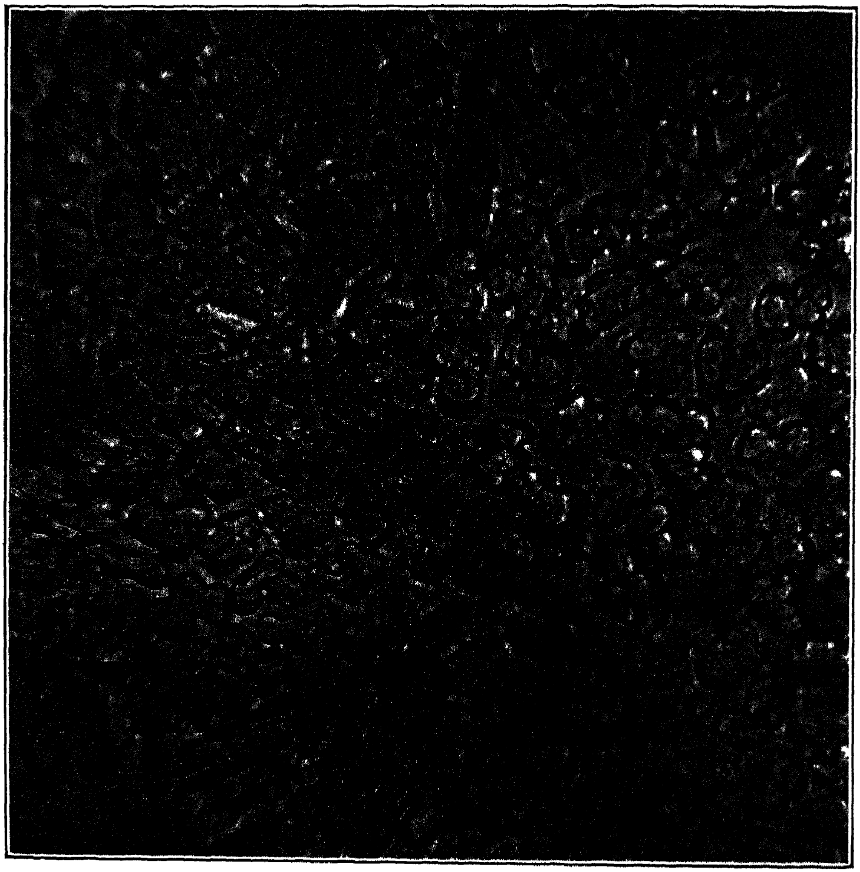


FIGURE V
Cross-section of Celanese
*Courtesy Associated Knit Underwear Manufacturers of America*

rayon, increasing in volume at the same time by about 40 per cent. When dried, it contracts and regains its previous volume and tensile strength. He explains the hygroscopic capacity of the older rayons as due to their capillary structure.

TABLE XV

TENSILE STRENGTH AND ELONGATION OF SILK AND RAYONS[9]

| | *Tenacity in Grams per Denier* *Dry* | *Wet* | *Per Cent Elongation* |
|---|---|---|---|
| Natural silk | 2.5 | 2.0 | 21.0 |
| Cuprammonium silk | 1.3 | 0.5 | 12.5 |
| Nitro silk | 1.48 | 0.31 | 15.5 |
| Viscose silk | 1.75 | 0.75 | 20.0 |

TABLE XVI

LOWER LIMIT OF STRENGTH AND STRETCH FOR THE BEST GRADES OF RAW SILK AND TYPES OF RAYON[7]

| | *Strength in Grams Per Denier* | *Stretch in Per Cent Elongation* |
|---|---|---|
| Raw silk | 3.50 up | 20 up |
| Regenerated rayon from cotton linters | 1.70 up | 20 up |
| Regenerated rayon from wood pulp | 1.50 up | 20 up |
| Acetate silk | 1.30 up | 30 up |

TABLE XVII

STRENGTH AND STRETCH OF VARIOUS RAYONS

| | *Number of Threads* | *Denier Size* | *Strength in Grams Per Denier* | *Stretch in Per Cent Elongation* |
|---|---|---|---|---|
| *Regenerated Cellulose Rayon from Wood Pulp* | | | | |
| American I, Factory No. 1 grade A | 100 | 150 | 1.56 | 27.5 |
| American II, Factory No. 1, Grade A | 200 | 150 | 1.54 | 28.5 |
| American III, Factory No. 2, best grade A | 200 | 150 | 1.60 | 24.5 |
| American IV, Factory No. 3, best grade A | 200 | 150 | 1.56 | 23.0 |
| European, grade not known, | 200 | 150 | 1.48 | 20.0 |
| European, grade C | 100 | 120 | 1.42 | 23.0 |
| *Regenerated Cellulose Rayon from Cotton Linters* | | | | |
| European, grade not known, | 200 | 80 | 1.63 | 21.5 |
| European, grade not known, | 100 | 300 | 1.56 | 20.0 |
| American Factory No. 1, best grades | 200 | 150 | 1.76 | 20.0 |
| American Factory No. 2, best grades | 200 | 150 | 1.85 | 22.0 |
| *Acetate Rayon* | | | | |
| European | 200 | 150 | 1.30 | 29.0 |
| European | 50 | 300 | 1.20 | 36.0 |

TABLE XVIII
SHOWING THE AREA, TENSILE STRENGTH, AND ELASTICITY OF THE VARIOUS RAYONS[10]

| *Type* | *Mean Area of Cross Section of Fiber in Sq. in.* | *Tensile Strength in Grams, Calc. for 100 Sq. in. Cross Sectional Area* | | *Elasticity in Per Cent Calc. for 100 Sq. in. Cross Sectional Area* | |
|---|---|---|---|---|---|
| | | *Dry* | *Wet* | *Dry* | *Wet* |
| Degummed Italian silk | 109 | 7.1 | 6.7 | 13.2 | 15.9 |
| Cuprammonium | 105 | 3.1 | 2.3 | 7.9 | 11.5 |
| Viscose I | 387 | 3.2 | 1.8 | 3.0 | 2.0 |
| Viscose II | 596 | 3.1 | 1.5 | 2.3 | 2.2 |
| Viscose III | 498 | 2.7 | 1.2 | 2.8 | 2.1 |
| Chardonnet T I | 584 | 3.9 | 2.2 | 3.5 | 2.6 |
| Chardonnet T 2 | 424 | 2.7 | 1.4 | 3.5 | 2.4 |
| Chardonnet T 3 | 728 | 2.6 | 1.7 | 2.6 | 1.7 |
| Chardonnet S. KZ | 225 | 3.3 | 2.3 | 3.6 | 3.2 |
| Acetate | 447 | 1.8 | 1.5 | 6.1 | 5.4 |

According to Oppe and Gotze,[11] viscose silk increases in length about 0.6 to 0.8 per cent with an increase in the humidity of the atmosphere from dry air to 3.5 per cent relative humidity. An increase in the relative humidity from dry air to 83 per cent relative humidity gives an increase of from 1.1 to 1.5 per cent in the length of viscose. It is interesting to note that, while acetate silk absorbs a far smaller amount of moisture under the same conditions, it does not show any notable variations in length, at the various humidities, from the other varieties of rayon.

### *Alkalies and Acids*

The resistance towards alkalies varies with the product, Celanese being considerably more sensitive than Lustron, but neither should be allowed to come into contact with strongly alkaline solutions, especially when hot, except under special conditions, otherwise both become blind, curly and wool-like. However, in spite of this, fabrics containing either Lustron or Celanese may be mercerized under the proper conditions.

For example, British Patent No. 210,484, October 5, 1922, to W. Marshall[d] states that cotton yarns in mixed fabrics containing

[d] United States Patent No. 1,511,741, October 14, 1924, to W. Marshall covers the same process, which gives excellent results on piece goods, etc. The dyeing properties of the acetate silk are almost unaffected, except that it acquires more affinity for certain direct dyes. The same process may also be used for the production of crepe effects by mercerization without tension.

acetate silk and unmercerized or incompletely mercerized cotton may be mercerized by treatment with a sodium hydroxide solution of 1.24 to 1.30 specific gravity at a temperature below 15° C. (59° F.). The fabric should then be squeezed between rollers, stretched,

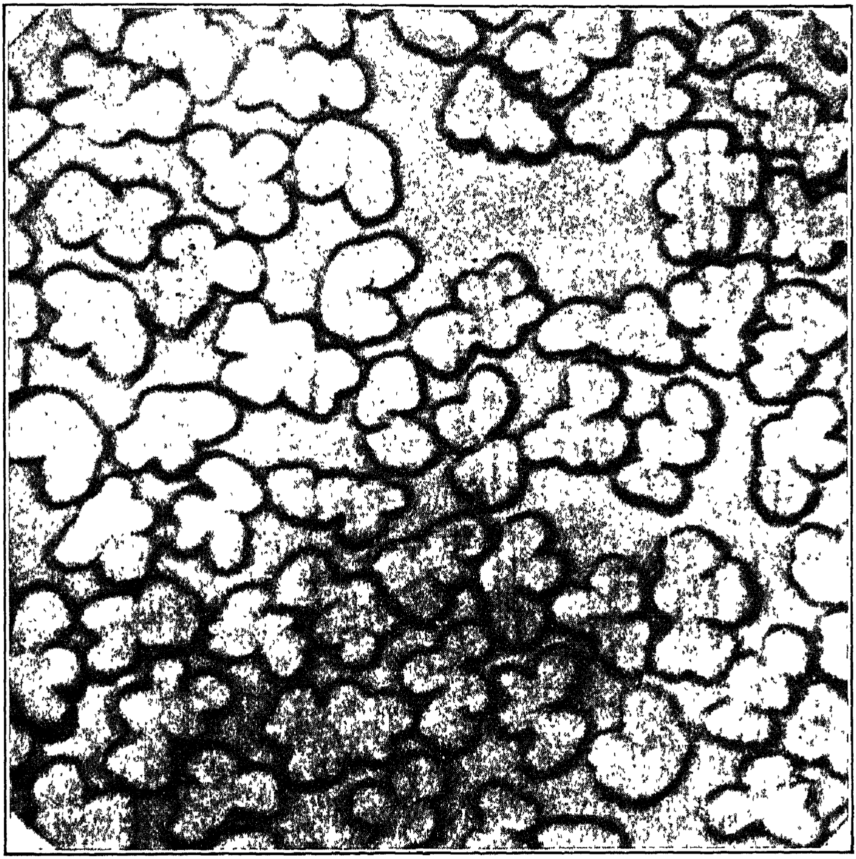


FIGURE VI
Cross-section of Rhodiaseta
*Courtesy Societe pour la Fabrication de la Soie "Rhodiaseta"*

washed, treated with dilute acid, and washed until neutral. During this treatment the acetate silk does not lose its luster or shrink, the loss in weight is very slight, and its dyeing properties are not materially affected. In order to avoid a crepe effect, the fabric should be mercerized under tension. This or a similar process is now in use in several plants.

While the above patent probably applies particularly to Celanese, Lustron in combination with cotton will also withstand the mercerizing process on the usual mercerizing range with sodium hydroxide solution of 13 to 15 per cent strength at temperatures below 5° C. (40° F.) without loss of its cross-dyeing properties, and with proper care will even withstand the action of a 35 per cent sodium hydroxide solution at 15° C. (60° F.) for a short time. After mercerizing, the union should be rinsed as before, and the remaining alkali neutralized with dilute acetic acid, never with mineral acids. The dilute acid remaining in the fabric may be neutralized with sodium bicarbonate if the goods are not to be used immediately. In case the mercerizing is not done on a machine, contact with the mercerizing solution should not exceed 45 seconds.

Towards mineral acids, the resistance of acetate silk is not as great as that of the older rayons. Little[12] states that acid hydrolysis affects acetate silk in much the same manner, in the initial stages, as saponification (alkaline hydrolysis); but upon being carried to the extreme, there is an actual disintegration of the fiber very similar to that which occurs in the case of cotton when sulfuric acid is left in it.[e] This of course means complete destruction of its textile properties.

The manufacturers of Celanese warn against the use of alkalies, but state that it will withstand the usual alkaline emulsion finish, or an acid finish containing 2 cubic centimeters per liter of formic acid. The Lustron Company advise against the use of sulfuric acid in any process on their product, suggesting the substitution of formic or acetic acid. They also state that no matter what the dyeing process has been, the last wash water should contain about 0.5 ounce of sodium bicarbonate per gallon of water, and the goods should be wrung and dried without further rinsing. Finishing materials for Lustron should be slightly on the alkaline side. In the presence of strong oxidizing agents, acetate silk forms oxycellulose.

Prof. Johnson[13] found that upon boiling the four types of rayon for fifteen minutes with 15 per cent of sodium hydroxide, wash-

[e] This probably applies particularly to Lustron which is more sensitive to mineral acids than Celanese.

ing thoroughly, neutralizing in very dilute acetic acid, and washing acid free with water, nitro silk was disintegrated; but acetate and viscose silks held up better. Upon treating 150 or 300 denier rayon yarns for 15 minutes in a 5 per cent solution of sodium hydroxide at 82 to 93° C. (180 to 200° F.), then washing, neutral-

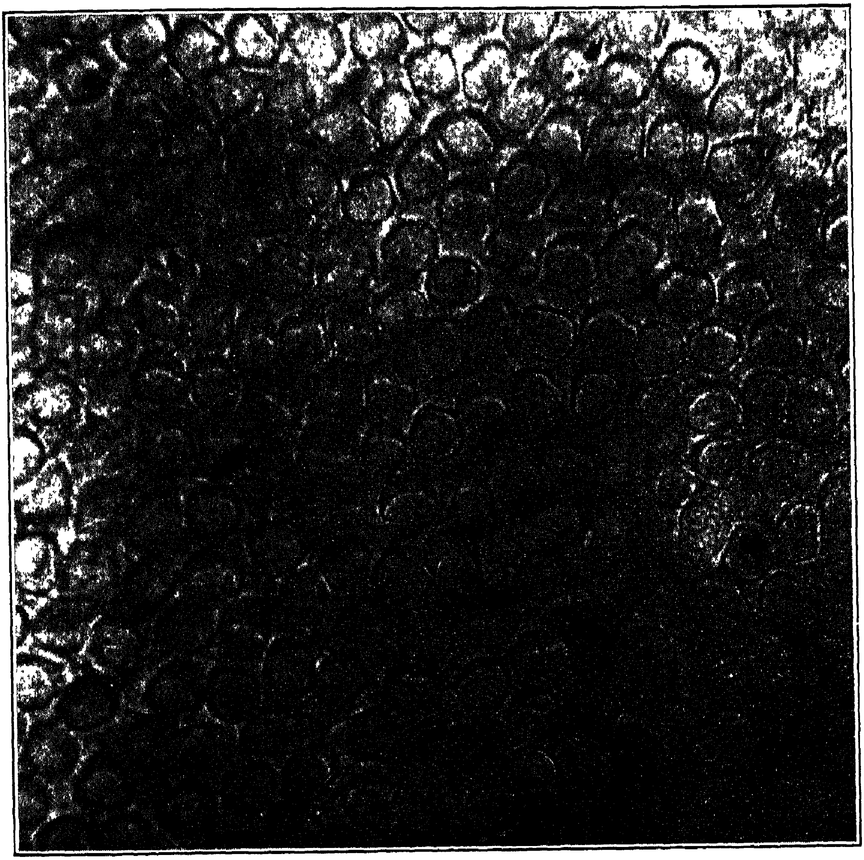


FIGURE VII
Cross-section of Cuprammonium Silk
*Courtesy Associated Knit Underwear Manufacturers of America*

izing, and washing as above, finally rinsing in 95 per cent alcohol, then in ether, and drying at 110° C., the various rayons lost weight as follows: nitro 8.41 per cent, viscose 2.26 per cent, cuprammonium 3.96 per cent, Celanese 53.0 per cent, and Lustron 64.0 per cent. The Lustron and Celanese yarns were largely reduced

to a slimy mass. While wool was completely dissolved in from 3 to 5 minutes by the above treatment, raw true silk and Tussah silk did not completely dissolve in 5 minutes.

### *Luster and Blinding*

In his report upon the rayons in use about 1900, Hassac[31] states that the Pris de Vaux, Fismes, and Lehner samples (see Table VI) were very similar in appearance and more lustrous than true silk. The Walston sample was rough and hairy, resembling mohair rather than silk. The cuprammonium silk resembled the Pris de Vaux and Fismes samples, with a higher luster, and the feel of true silk when in the piece. When wet out with water, the Pris de Vaux, Walston, and Fismes samples under the microscope at 150 diameters appear very similar, the last named being more deeply grooved. The Pris de Vaux had the most symmetrical outline in cross section, and the Fismes the least symmetrical. The Lehner was characterized by deep longitudinal grooves, and by small air bubbles, its cross section being very irregular. The cuprammonium had fine longitudinal grooves, and minute transverse lines in the center of the fiber cross section. Its cross section was regular, approaching a circle or ellipse. The gelatin silk was almost circular in outline and free from grooves and bubbles, the fracture even and the thickness constant. In polarized light the gelatin silk was singly refractive, while the others were doubly refractive. The cuprammonium showed uniform interference colors over considerable lengths of fiber. In the Pris de Vaux, Fismes, Walston, and Lehner samples, the colors varied greatly owing to the irregular thickness of the fibers.

Dr. Luft[9] describes the luster of the various rayons as follows: nitro is shiny and cuprammonium glassy, while viscose and acetate are silvery and more in the nature of true silk. Cuprammonium silk is generally more milky than viscose, but the latter also has a milky appearance at times. The feel of rayon is similar to true silk but slightly colder and harsher to the touch. The scroop of natural silk may be imitated on rayon by an acid finishing process. Acetate silk does not lose its sheen or silky feel on washing, or turn yellow with age, sunlight, washing, wear, or perspiration. It

drapes well and Celanese is stated to be more regular in denier than any other variety of commercial rayon.

The loss of luster by Celanese and related acetate silks (but not Lustron) when overheated in the presence of water vapor or in most aqueous solutions, especially in the presence of alkalies, has

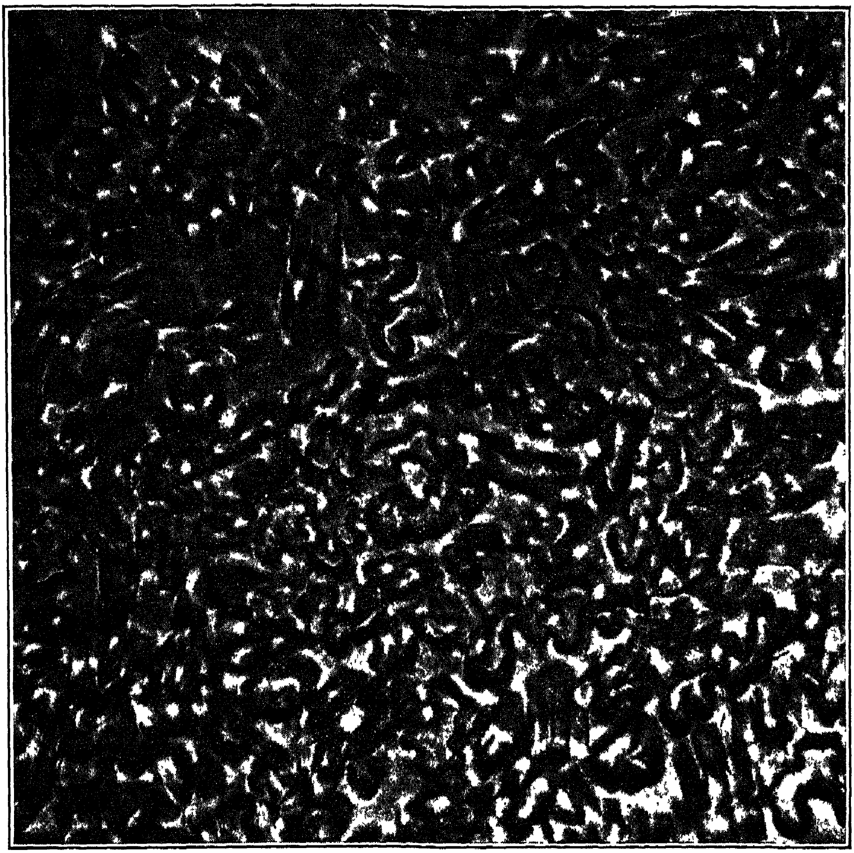


FIGURE VIII
Cross-sectoin of Tubize Silk
*Courtesy Associated Knit Underwear Manufacturers of America*

been mentioned quite frequently in the foregoing pages. This phenomenon is also known as "blinding" and may be due to any one of a number of causes, such as an acid-bichromate treatment,[15] as in mordanting wool; the action of certain metallic salts, such as the chlorides of copper, calcium, magnesium, etc.; or improper

handling during the development of certain diazotized colors on the fiber, in which case the coloring matter appears to be precipitated near the surface of the fiber.

Very probably this blinding is due to a loss of acetate groups by the cellulose acetate, possibly due to the hydrolysis of the ester at the higher temperature. This theory is supported by Greenhalgh[14] who states that it is not due to physical causes, and by the fact that this blind fiber may be relustered by an appropriate treatment with an acetic acid solution of suitable strength.[f] This effect is probably due to dehydration in the presence of a solvent of higher boiling point than water. It may be that the superior hot water resistance of Lustron is mainly due to two cases; i.e., the presence of a larger proportion of combined acetic acid groups, so that a larger number may be removed before the luster is impaired, and to the presence of neutralized sulfuric acid group, which Caille[16] reports greatly increases the resistance of the fiber to hydrolysis in hot water.

As may be expected, any operation on acetate silk which interferes with, or impairs its luster, has the tendency to reduce the brilliancy of the color of the dyed fiber. In most cases there appears to be a definite relation between the luster of the fiber and the brilliancy of the dyed shade and very probably if we were able to apply to cotton the dyes giving the most brilliant shades on acetate silk, the resulting brilliancy of shade would not be at all the same.

*Temperature*

The resistance of Lustron to dry heat[12] is similar to that of viscose, true silk, or cotton, either at high temperatures for short periods, or low temperatures for a longer time. Wherever possible it should be dried at a low temperature.[g] At temperatures above about 225° F., Celanese becomes glazed and brittle. As previously mentioned, at temperatures above about 85° C. (185°

[f] Also see other methods of relustering acetate silk in Chapter XXXVIII.

[g] United States Patent No. 1,607,474, November 16, 1926, to H. S. Mork of the Lustron Company states that cellulose acetate and acetate silk are rendered more stable to the action of heat, carbonization being inhibited, by incorporation, before or during the manufacturing process, of 0.5 to 2.0 per cent of the potassium or sodium salt of acetic, oleic, salicylic, benzoic, or other suitable organic acid.

F.), in the presence of water, as in dyeing, Celanese and Rhodiaseta become "blind" unless special precautions are taken to prevent this, such as the presence of certain suitable inorganic salts.[h] On treating Celanese with boiling water, it shrinks, becomes curly and wool-like, and the luster is completely destroyed in a

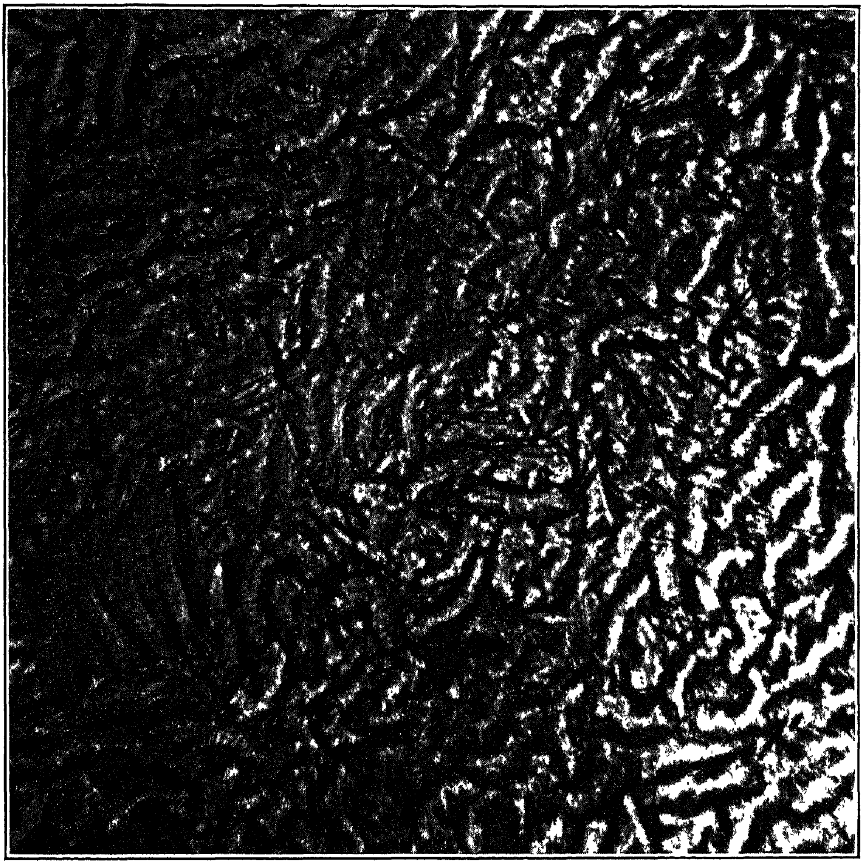


FIGURE IX
Cross-section Du Pont Silk
*Courtesy Associated Knit Underwear Manufacturers of America*

few minutes. Hot ironing with a damp cloth also injures Celanese, but dry steaming for say 15 minutes, without pressure, does not seriously damage it and this process is sometimes used in

[h] See British Patents No. 206,113 and No. 246,879.

printing Celanese fabrics. On the other hand, Lustron can be treated in boiling water without affecting its luster or general appearance. This enables it to go through a regular silk boil-off and dyeing at boiling temperatures without alteration of its appearance.

### *Flammability*

According to a recent article in the *Technical News Bulletin*, tests made at the United States Bureau of Standards indicate that cuprammonium silk is the only rayon which ignites more easily than cotton, but this difference is very slight. Viscose ignites at approximately the same point as cotton, while the nitro is less susceptible to ignition than cotton. Acetate silk is even less susceptible to ignition than the nitro.

### *Microbiological and Electrical Resistance*

Thaysen and Bunker[17] investigated the resistance of the four commercial varieties of rayon to certain cellulose destructive organisms. Tests were made (1) in an anaerobic medium, (2) by burying in garden soil, and (3) by submerging in sea water. Acetate silk was found to be the most resistant. The resistance of the older rayons varied in the following order: nitro, viscose, and cuprammonium.

The unusually high resistance[33] of cellulose triacetate to hydrolysis by enzymes is lost when the ester is saponified, and the regenerated cellulose is hydrolyzed about 35 times more than the normal unacetylated cellulose by the enzyme of snails.

The electrical resistance of acetate silk is greater than that of any other known fiber, especially in a damp atmosphere, and for this reason it is rapidly displacing real silk for electrical insulating purposes in many places.

### *Specific Gravity*

Chardonnet in 1889 gave the specific gravity of rayon prepared from collodion (nitro silk) as 1.49, raw silk 1.66, and boiled-off silk as 1.43. Herzog[18] gives the specific gravity of Chardonnet silk as 13 per cent higher than that of true silk, which on a basis of 1.43 for true silk, would be about 1.62. Silberman[19] states that

Lehner's silk (nitro) should be 7 to 8 per cent heavier than true silk, (1.43 plus 8 per cent) or 1.545 sp. gr. The specific gravity of cuprammonium silk is greater than that of nitro or viscose. Hassack,[20] and Saget and Suevern[21] report the specific gravity of

FIGURE X
Cross-section Industrial Fiber
*Courtesy Associated Knit Underwear Manufacturers of America*

natural silk as 1.36, and that of the rayons as 1.50 to 1.53. Worden[22] gives the specific gravity of acetate silk, probably Lustron, at 1.25. The specific gravity of Rhodiaseta is 1.27. Luft[9] gives the gravity of cellulose rayon (variety not stated but probably viscose) as 1.5, and that of true silk as 1.4.

TABLE XIX

Specific Gravity of Different Rayons of about 1900[31]

| | |
|---|---|
| Natural silk | 1.36 |
| Pris de Vaux silk (Chardonnet) | 1.52 |
| Fismes silk | 1.52 |
| Walston silk | 1.53 |
| Glattbrugg silk (Lehner) | 1.51 |
| Glanzstoff silk | 1.50 |
| Gelatin silk | 1.37 |

### *Refractive Index*[1]

The refractive index of acetate silk, as compared with the other rayons and natural fibers, is low. This applies to the older chloroform soluble (primary) type as well as the newer acetone soluble (secondary) variety. Herzog[23] reported the refractive index of acetate silk as 1.474 to 1.479, with sodium light. Judging from the date, this was undoubtedly a primary acetate. Recent work by the author indicates that this figure checks fairly well for both Lustron and Celanese of today. Acetate silk is more transparent to ultraviolet light than any other fiber.

### *Structure*

Herzog, who has made a considerable investigation on the structure of various materials by means of X-rays, in a joint paper with Jancke,[24] states that from their experiments with X-rays they believe that in plant fibers the cellulose is present in crystalline form, dispersed symmetrically with respect to the axis of the fiber. Natural silk also shows the symmetrical crystalline structure. The rayons, with the exception of acetate, consist of an irregular felted mass of crystalline fragments of unchanged cellulose. Acetate silk is amorphous and consists of a mixture in which the cellulose acetate has undergone considerable degradation. Animal hair is also amorphous and probably consists of two or more substances, while starch and pure fats are crystalline.

Ott[25] contradicts the statements of Herzog and others that the X-ray diagrams of cellulose triacetate show it to be amorphous. His diagrams show a crystalline structure but the interference

[1] Also see Identification of Rayons.

bands are rather blurred, owing to the minute character of the crystals, and their low intensity may account for their having been overlooked previously. Probably this fine crystalline structure explains the low porosity of acetate silk.[j]

According to Hess, Schultze and Messmer,[26] Bayer's "Cellite,"

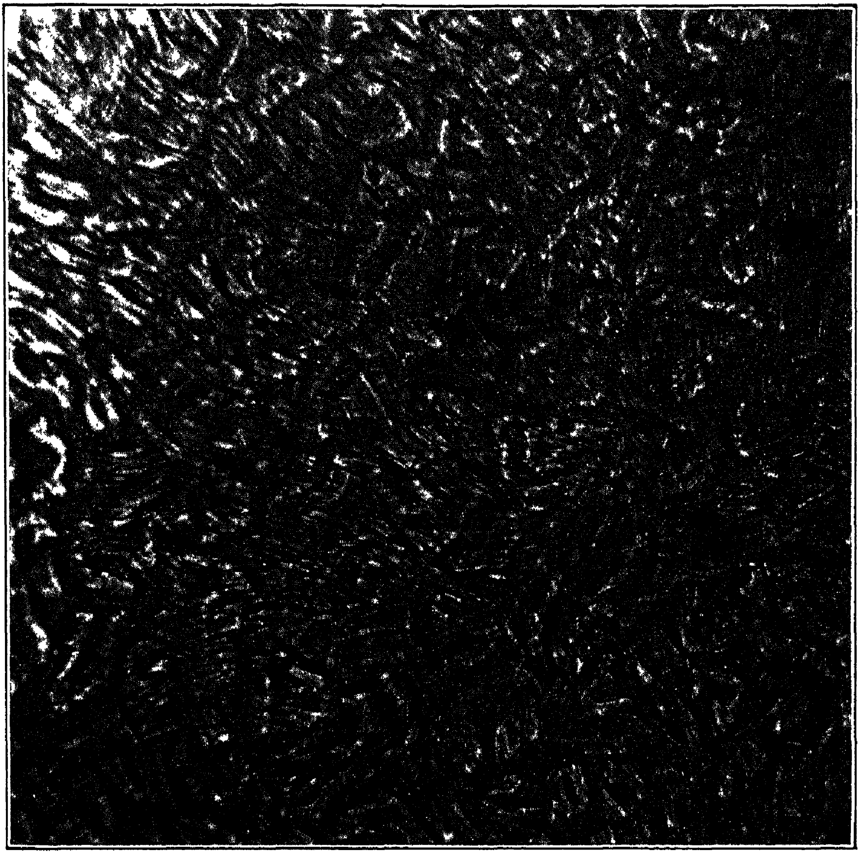


FIGURE XI
Cross-section Viscose Silk.
*Courtesy Associated Knit Underwear Manufacturers of America*

which is soluble in acetone but insoluble in chloroform, and is prepared by the partial hydrolysis of cellulose triacetate with sulfuric and acetic acids, as in German Patent No. 252,706, consists of a

[j] Herzog[34] reports that both cellulose acetate and nitrate have a rhombic structure.

mixture of cellulose triacetate and isomeric diacetates in the ratio of 1 to 4, together with dextrose and cellobiose. After about six precipitations from benzene-alcohol, the mixture of tri- and di-acetates shows signs of crystallization, and well defined crystals

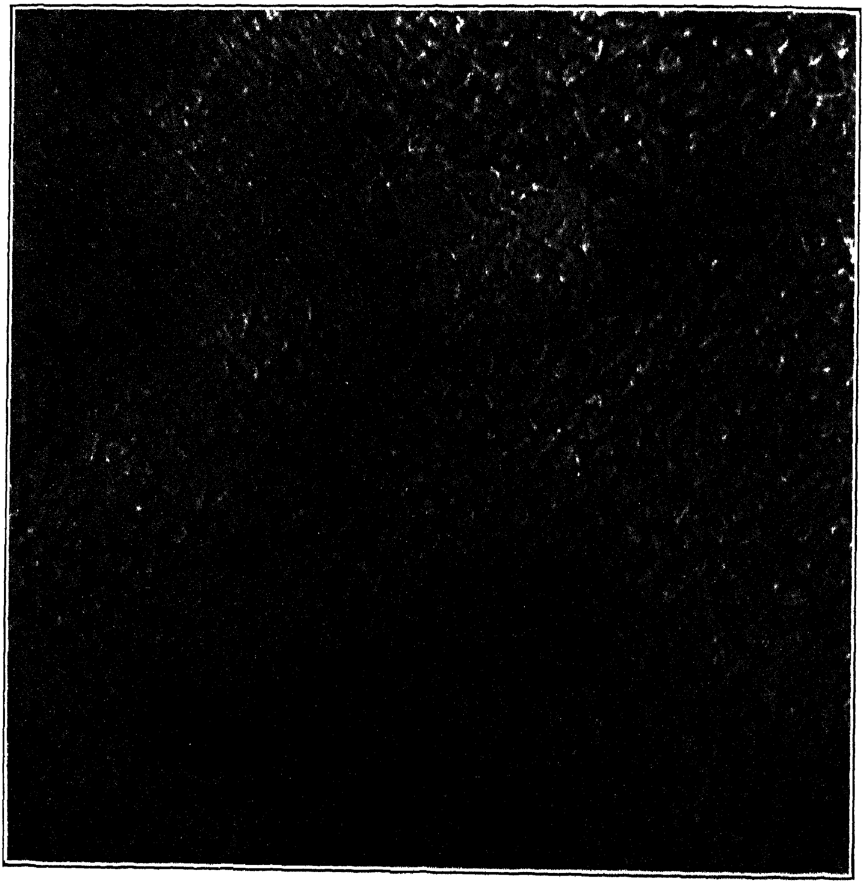


FIGURE XII
Cross-section of True Silk
*Courtesy Associated Knit Underwear Manufacturers of America*

are eventually obtained. These are stable only in contact with the solvent and become amorphous when dry. Like the triacetate crystals, they show no X-ray line spectrum. The rotary power curves indicate that the crystalline acetate is derived from chemi-

cally intact cellulose, and it is impossible to separate the cellulose into isomerides by prolonged fraction crystallization or chloroform extraction of the di- and triacetates.

Microscopic examination[27] of the cross section of viscose silk shows corrugations similar to the bark of a tree and the individual fibers interlock each other due to these corrugations, the result

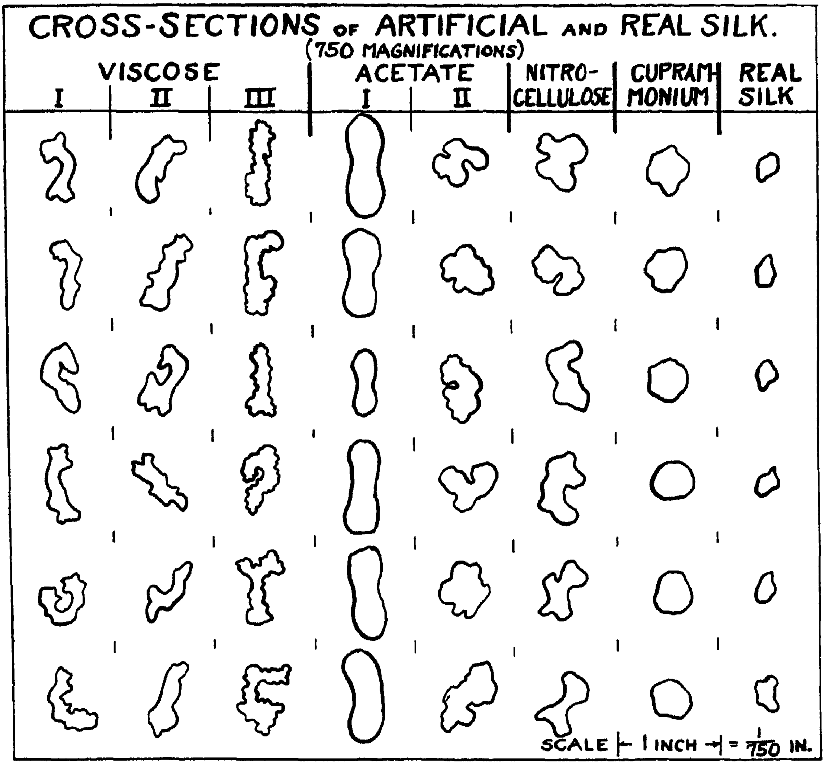



FIGURE XIII
A Comparison of the Cross-section of the Various Rayons. Under Acetate Silk, No. I is Lustron and No. II is Celanese
*Courtesy Associated Knit Underwear Manufacturers of America*

being greater strength and covering power. The cross section of acetate (variety not stated) and cuprammonium silks show no corrugations, the former being more oval, and the latter one round and of uniform diameter. Nitro silk is more oval than viscose and shows only slight corrugations. Very probably the micro-

scopic cross section of any one kind of rayon will vary considerably with the differences in details of manufacturing methods, such as the dry spinning and wet precipitation methods used in the manufacture of acetate silk. The accompanying figures show the microscopic characteristics of the various rayons.

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# CHAPTER V

# THE IDENTIFICATION OF THE RAYONS

*A Discussion of the Various Properties and Tests Used in Identifying the Different Rayons*

BEFORE attempting to dye or, in fact, to conduct any other process on rayon or materials containing it, the dyer should know exactly the variety of rayon he has to handle. As mentioned before, each different process of rayon manufacture produces a product which differs in some points from all other rayons and fibers. In the case of acetate silk, the product differs widely from all other commercial fibers in many ways. These very differences form the basis of the many ways of identifying the products of the various methods of rayon manufacture. Of course the point which is of major interest to the dyer is their differences in dyeing properties, such as dyestuff affinity, fastness, exhaustion, etc. Most dyers are so familiar with the older rayons that once they are identified, they know how to handle them.

While a number of methods for the detection of rayon, as well as the identification of the particular variety present, have appeared in the literature, no one of these methods is applicable in every case to give the full details usually necessary to the dyer. The differences between the rayons on one hand, and true silk or mercerized cotton on the other, show up readily under the microscope, while the differences between rayon, cotton, linen, wool, etc., are plainly visible to the eye alone. However, it is difficult to identify the variety of rayon even under the microscope, which is not always available, so that chemical tests are also necessary. The methods of detecting mercerized cotton, as well as estimating the degree of mercerization, will be dealt with in another chapter.

### *Solubility Tests*

One of the simplest and easiest tests of individual fibers for acetate silk (Lustron,[a] Celanese and Rhodiaseta) is its solubility

[a] While Celanese and Rhodiaseta dissolve completely in acetone, Lustron does not, but is soluble in chloroform, whereas Celanese and Rhodiaseta are not completely soluble in chloroform.

in acetone. Warming hastens the solution, although they are also soluble cold within a short time. The fact that this method may be used upon either white or properly dyed acetate silk gives it a considerable advantage over the colorimetric tests. However, if the acetate silk has been saponified in dyeing or otherwise, it will not be completely soluble in acetone. But if the acetone solution is evaporated, a film of cellulose acetate will remain, showing the presence of this compound.

It is also more or less soluble in warm 65 per cent or stronger acetic acid, particularly glacial acetic acid. The older regenerated cellulose rayons are not soluble in either acetone or acetic acid. It has been shown by Prof. Johnson[1] that there is some difference in the solubility of Lustron and Celanese in acetic acid. Near the boil, 30 cubic centimeters of 50 per cent acetic acid will dissolve 0.05 gram of Celanese, while under the same conditions, it requires the same amount of 65 per cent acetic acid to dissolve Lustron.[b] Furthermore, upon pouring the 30 cubic centimeters of acid containing the Celanese into 15 cubic centimeters of water, a bulky opaque mass is obtained which soon forms a flocculent sediment. Upon diluting the Lustron solution in a similar manner, only a slight opaqueness and some evidence of a translucent sediment are obtained. Where this test is made upon white acetate silk, the precipitate is white, but where the colored fiber is used in testing, the precipitate is frequently colored.

Acetate silks prepared from the older primary cellulose acetates are soluble in chloroform, while the later secondary cellulose acetate silks are only more or less plastic in chloroform alone, but are soluble in acetone. While Lustron is soluble in chloroform, Celanese only forms a jelly in this solvent and not a complete solution.[10] Both varieties are soluble in glacial acetic acid, as well as more slowly in cold concentrated sulfuric acid. Acetate silk is soluble in tetrachlorethane and alcohol while the other rayons are not. Undenitrated Chardonnet rayon is soluble in cold amyl acetate. The solubility of acetate silk in other solvents is discussed further in Chapter III.

[b] This is not the limit of solubility but is merely used for the purpose of this test and indicates the difference in the strength of acid required to dissolve the two varieties.

*Ammoniacal Copper Oxide Solution*

Acetate silk is swelled by, but is not soluble in, ammoniacal copper oxide solution (Schweitzer's reagent), while the older rayons swell and dissolve, as also does fibroin (true silk). This reagent should be freshly prepared by dissolving 5 grams of copper sulfate crystals in 100 cubic centimeters of boiling water and adding sodium hydroxide solution until the precipitation is complete. Wash the precipitated copper hydroxide free of alkali and dissolve it in the least possible quantity of concentrated ammonium hydroxide solution. It is best preserved away from light.

*Chromic Acid*

A half-saturated solution of chromic acid dissolves true silk slowly, and the older rayons in the cold, while acetate silk only swells and is not dissolved. This reagent is prepared by mixing potassium bichromate with an excess of sulfuric acid. Crystals of chromic acid separate. These are removed and dissolved in water to give a saturated solution, which is diluted with an equal volume of water for use.

*Water and Alkali Tests*

Acetate silk does not swell in water, while all other rayons are turgoids and swell to some extent. Some of the recently proposed treatments for preserving the strength of the older rayons when wet may affect this swelling of the older rayons to some as yet unknown degree. The older rayons also lose a larger proportion of their dry strength when wet than does acetate silk. The acetate silks do not withstand the action of hot sodium hydroxide or other strongly alkaline solutions, in which they lose luster, as described in Chapter IV. The other rayons withstand this treatment better than acetate. They all swell to some extent, but none dissolve, so that this test will readily serve to distinguish the rayons from true silk and wool.

*The Burning Test*

Another very simple test is the burning test which has been widely recommended for distinguishing the acetate silks from all other fibers. In making this test the fibers should be rolled into a tight little ball or wad and placed near the flame without touching it. With sufficient heat the acetate silk appears to melt rather than

burn, in somewhat the same manner as sugar, forming a black globule which precedes the small flame down the thread. Upon extinguishing the flame, the small lump on the acetate silk is rather hard.

Cotton burns with a flash,[21] little odor and almost no ash. Nitro, viscose and cuprammonium silks readily burn, like cotton, without melting, and leave almost no ash, which is soft. Vegetable fibers sometimes leave a slight ash in the form of the thread. The smoke has the odor of burning paper and turns moistened blue litmus paper red.

Wool and silk are readily distinguished from the natural and artificial cellulose fibers, such as cotton, linen, rayon, etc., in the burning test. The animal fibers leave a shining, tumefied, difficultly combustible cinder, which leaves considerable ash when completely burned. The smoke has the characteristic odor of all burning nitrogenous animal matter, and turns moistened red litmus paper blue.[c] It also turns tumeric paper brown. Wool and silk may also be distinguished from the rayons and vegetable fibers by the yellow color developed when steeped in either nitric or picric acid solution, the cellulosic fibers remaining white.

According to Clayton[2] when a heavy cord of Celanese is placed near, but not in, a Bunsen burner flame, as the temperature rises the color of the fiber changes from white to yellow and yellowish-brown, finally becoming brittle, almost like a stick of sugar which has been heated to its melting point and allowed to cool. When in direct contact with the flame a slow burning action occurs with the formation of a black molten pellicle at the burning end. More or less charred globules may fall from the end of the burning Celanese yarn, especially if it is held intermittently in a vertical plane over the burner. He states that when cellulose acetate is heated in the air, it is gradually converted into a semi-liquid phase (possibly slightly beyond the point at which decomposition begins) and further heating causes its more or less complete decomposition. Cotton and the other rayons do not pass through a liquid phase upon heating in the presence of air. Acetate silk quickly loses its tensile strength at elevated temperatures, as do also wool and true

[c] Where the regenerated rayons have been sized with gelatin or glue this may give a nitrogenous odor on burning and cause it to be confused with true silk or wool.[22]

silk but to a less extent, and this may serve as a quick test to distinguish it from the other rayons and cotton. One or two passes above a Bunsen flame is usually sufficient to disrupt acetate silk yarn or cloth.

*The Acetate Test*

The "acetate test" has frequently been recommended as a test for acetate silk. Possibly the best method of making this test is to dissolve the fiber in a little chloroform and boil this solution with a normal solution of sodium hydroxide. Dilute with water, and filter off the precipitated cellulose and evaporate the solution just to dryness. Add sufficient water to dissolve the residue and acidify with sulfuric acid. Add a little ethyl alcohol and the same amount of concentrated sulfuric acid, warm, and if the sample contains acetate silk, the odor of ethyl acetate may be detected.

Trotman and Trotman[16] suggest boiling the rayon sample with a solution of potassium hydroxide, when potassium acetate is formed in the presence of acetate silk. This filtered solution may be concentrated, carefully neutralized, and a little neutral solution of ferric chloride added. If acetate silk was present, the red color of ferric acetate is apparent and upon boiling, a red precipitate of basic ferric acetate is formed, while acetic acid is liberated and its odor may be detected.

As a shorter test, the filtered potassium hydroxide solution, after boiling the sample, may be concentrated to a small volume, cooled, and acidified with sulfuric acid. If the sample contained acetate silk, the characteristic odor of acetic acid is present on warming.

*The Acetamide Test*

Clayton[2] proposes the acetamide test, when other methods fail, for acetate silk. This may be used on either white or dyed fibers. A hard glass test tube is drawn out near the middle, so that the opening left can be subsequently closed quickly with a suitable flame. A few strands of the fiber are introduced into the tube and ammonia added to about one-tenth the capacity of the tube. Before sealing the tube, the ammonia should be heated gently to drive out most of the air, and if possible the fibers are arranged in the upper portion of the tube as sealed. The tube is then sealed,

surrounded by a safety screen, and the lower portion placed in a suitable oil bath, the temperature of which is slowly raised to about 120 to 140° C., and held at this temperature for 30 to 60 minutes. On cooling the tube and opening it, the odor of a small amount of impure acetamide will be detected, if the fiber sample contained acetates.

### *Distinguishing Lustron and Celanese*

Perhaps the most complete paper upon the identifiation of the rayons is that of Prof. Johnson.[1] In addition to the acetic acid test just mentioned, he recommends the following reagents:

1. Diphenylamine; a 1 per cent solution in concentrated chemically pure sulfuric acid.
2. Various dye solutions; 1 part of dyestuff in 1000 of water.
   - *a.* Methylene Blue.
   - *b.* Pontamine Scarlet B, or its equivalent.
   - *c.* Sulfur Khaki Y, or its equivalent.
3. Millon's reagent: Dissolve metallic mercury in its own weight of chemically pure concentrated nitric acid and then dilute with an equal volume of water.

Before making the colorimetric tests upon dyed rayon, it is usually necessary to "strip" the color from the fiber. This may be done by the usual methods with hypochlorite, peroxide, permanganate, hydrosulfite or a hydrosulfite-formaldehyde compound, such as Protolin AZ, in a solution containing acetic or formic acid. The latter method is recommended, but will not remove all dyes from acetate silk.[d] Care must be observed that the stripping operation does not so alter the rayon as to obviate the results of the identification tests. Samples for testing should be of a white color, if possible, and free from sizing, oils, bleaching, or other chemicals or foreign matter.

### *Dyeing Tests*

Lustron and Celanese may be distinguished by boiling a few threads of the sample in 10 or 15 cubic centimeters of the 2*a* Methylene Blue solution as above, acidified with 1 or 2 cubic centi-

[d] Also see Chapter XXXV.

meters of acetic acid. Wash the dyed samples well in water. The Lustron retains a deep blue color, but the color of the Celanese washes out to a comparatively pale blue. This difference is entirely due to, and is typical of, the affinity of the two fibers for the basic dyes.[e] While the basic dyes have a greater affinity for Lustron than any other known textile fiber, this is decidedly not the case with Celanese. Dort[3] states that this test is not always reliable.

Ginsberg[4] states that if a rayon sample is placed in a solution of 3 per cent Methylene Blue and 2 per cent acetic acid, nitro silk will rapidly assume a marine-blue color, quickly exhausting the bath, while viscose and cuprammonium silks are only slightly dyed and leave the remaining bath thick. Acetate silk (probably Celanese) is not dyed, but after soaking in diluted alcohol or other suitable swelling solvents, the dyestuff is quickly absorbed into the fiber. If Lustron and Celanese are dyed together in the same dye bath at the same time with a basic dye such as Rhodamine or Malachite Green, the Lustron will take on a very full shade while the Celanese will show only a comparatively light shade. Celanese is claimed to have a slightly greater affinity for the Ionamines and S. R. A. dyes than Lustron and it has been stated that they may be differentiated by this test. None of the other rayons are dyed by either the Ionamines or dispersal dyes, however, some of them stain wool and true silk to some extent. The luster of Celanese and Rhodiaseta is impaired by boiling it in pure water, while Lustron withstands this treatment very well.

### *True Silk*

Upon treating the unknown sample with Millon reagent and warming gently, true silk is colored a brick-red, while all of the rayons, including acetate silks, are unstained. Animal fibers may also be identified by the fact that when boiled with a decolorized solution of magenta and afterwards well washed, they assume a pink color, while all other fibers are colorless. This reagent may be prepared by dissolving 0.1 gram of magenta (fuchsin) in 100 cubic centimeters of water and adding sulfurous acid solution until it is just decolorized. The sulfurous acid solution is conveniently

[e] This test should be used only in the proven absence of nitro silk.

prepared by dissolving sodium bisulfite in water and acidifying with hydrochloric acid.

*Ammoniacal Nickel Oxide Solution*

Ammoniacal nickel oxide reagent swells but does not dissolve either acetate or the older rayons. However, it dissolves true silk almost immediately. It is prepared in almost the same manner as the corresponding copper oxide reagent. Dissolve 5 grams of nickel sulfate in 100 cubic centimeters of water and add sodium hydroxide solution until the nickel hydroxide is completely precipitated. Wash the precipitate free of alkali and dissolve in 25 cubic centimeters each of concentrated ammonia and water.

*Alkaline Copper Solution*

Copper-glycerol reagent may also be used to distinguish between rayon and true silk. While it quickly dissolves the latter, it is without action on any of the rayons, including acetate silk. This reagent is prepared by dissolving 10 parts of copper sulfate in 100 cubic centimeters of water, adding 5 parts of glycerol and then sufficient concentrated aqueous potassium hydroxide to completely dissolve the precipitate at first formed. Of course, the acetate silks lose luster on warming in this reagent.

According to Formhals[5] true silk, even if weighted and dyed, may be distinguished from rayon by treating a small portion of the sample for a short time in a few cubic centimeters of concentrated sulfuric acid, diluting the mixture with water, adding sodium hydroxide to alkalinity, and then adding diazotized *p*-nitroaniline solution. Natural silk gives a red solution under these conditions, while the rayon solution is yellow. Very probably the presence of wool would also give a red solution, similar to silk.

*Nitro Silk*

Upon wetting a fiber of nitro silk with the diphenylamine solution, it is at once colored blue and dissolves in a few minutes. Another method suggested for identifying the nitro silk is to dissolve the samples in concentrated chemically pure sulfuric acid and add brucine sulfate to the solution. This gives a bright red color

when nitro is present. Undenitrated nitro silk is soluble in amyl acetate and very flammable.

Schwalbe[6] states that if 0.2 gram of rayon is heated in a test tube with 2 cubic centimeters of Fehling's solution, nitro silk imparts a green color to the solution, probably due to its oxycellulose content, while viscose and cuprammonium silks do not decolorize the solution under the same conditions. In some cases the nitro silk may have a yellowish to red copper oxide precipitate on the fiber.

### *Distinguishing Viscose and Cuprammonium Silks*

If true silk, acetate and nitro silks are absent, viscose and cuprammonium silks may be distinguished by comparative staining with the Pontamine Scarlet B (Johnson's 2*b* solution) or Sulfur Khaki Y (2*c*), both of which have a greater affinity for the cuprammonium than for viscose silk. In this test, as well as in all others, it is recommended to use standard samples of the rayons from known sources for comparison in running the tests. In dyeing with the scarlet, about 1 per cent of dyestuff, on the weight of the fiber, should be used. With the Khaki, use about 3 per cent dissolved with 2 to 4 times as much fused sodium sulfide as dyestuff. A 1 in 2000 solution of Naphthylamine Black 4B (Cassella, a mixture of C. I. Nos. 246 and 308) dyes cuprammonium[17] dark bluish-gray and viscose a light reddish-gray, or a light bluish-gray (linters ) from a hot neutral dye bath. It will be noticed under the ruthenium-red tests that, whereas viscose is colored a bright rose, cuprammonium remains almost colorless.

### *The Silver Tests*

Gotze[7] states that a 1 per cent ammoniacal silver nitrate solution colors viscose a distinct brown, while under the same conditions cuprammonium silk remains colorless. He attributes the brown color to a deposit of finely divided silver in or on the fiber and not to silver sulfide.

Rhodes[8] obtains better results with a reagent containing 1 per cent of silver nitrate, 4 per cent of sodium thiosulfate, and 4 per

cent of sodium hydroxide, than with Gotze's reagent. The reagent is prepared by dissolving each chemical separately in water, adding the silver nitrate to the sodium thiosulfate solution, and when the precipitate which at first forms has dissolved, adding the sodium hydroxide solution. This is brought to a boil and filtered. The sample should be immersed for one minute in the boiling solution, when viscose is colored a deep red-brown, while cuprammonium silk remains almost white. The color of the viscose sample is very similar to a 2.5 to 4 per cent Chlorazol Brown M (C. I. No. 420, B. D. C.) dyeing. Nitro silk is also stained by both the Gotze and Rhodes tests, very probably due to its sulfur content, from the denitrating process, but may readily be differentiated from viscose by the diphenylamine test. Table XX gives the results obtained by these two tests.

TABLE XX

Colors on Viscose, Cuprammonium and Nitro Silks by the Gotze and Rhodes Tests as Compared with Chlorazol Brown M[8]

| *Variety* | *Gotze Test Color* | *Rhodes Test Color* |
|---|---|---|
| Cuprammonium Silk | 0.0% Chlorazol Brown M | 0.0 % Chlorazol Brown M |
| Viscose Silk | 0.3% Chlorazol Brown M | 2.5 % Chlorazol Brown M |
| Vistra Silk | 1.0% Chlorazol Brown M | 4.0 % Chlorazol Brown M |
| Nitro Silk (denitrated) | 0.6% Chlorazol Brown M | 3.25% Chlorazol Brown M |

Harrison[9] used a thiosulfate silver solution as a test for oxycellulose, consequently, certain forms of cuprammonium which are known to contain oxycellulose, may become colored by this test but the shade is grayer or less brown in character. Rhodes[8] points out that this grayer color in the presence of oxycellulose indicates that the brown on viscose and denitrated nitro silks, both of which contain sulfur, is not due to a precipitation of colloidal silver but to the presence of sulfur in the fiber.

According to Kraise[17] the very fine viscose silks now on the market do not always give exactly the same colors in certain tests as the heavier fibers. He gives Table No. XX-A showing the colors on the various fibers by the different methods and recommends the Rhodes and Naphthylamine Black tests.

TABLE XX-A
COLOR TESTS ON VARIOUS RAYONS

| *Variety* | *Naphthylamine Black 4B*[17] | *Gotze*[7] | *Rhodes*[8] |
|---|---|---|---|
| Viscose, 7-8 den. | Light reddish-gray | Rust-brown | Very dark blackish-brown |
| Viscose, 4 den. | Light reddish-gray | Rust-brown | Lighter blackish-brown |
| Viscose (linters) 7-8 den. | Light bluish-gray | Light rust-brown | Still lighter blackish-brown |
| Cuprammonium 1-2 den. | Dark bluish-gray | Light yellowish-brown | Very light gray |
| Nitro | Light reddish-gray | Rust-brown | Very dark blackish-brown |
| Acetate | Light reddish-gray | Light brown | Bluish-black |

### *The Sulfide Test*

Schreiber and Hamm[20] recently found that the traces of sulfur compounds remaining in viscose silk cause it to give a sulfide test with lead acetate paper which is not given by cuprammonium silk. In making this test they recommend that a 5 gram rayon sample be placed in a flask with 100 cubic centimeters of water and 3 cubic centimeters of concentrated sulfuric acid. The mouth of the flask is closed with a diaphragm of filter paper saturated with a 10 per cent solution of lead acetate, and the flask heated over a moderately boiling steam bath for 4 hours. If at the end of this time the exposed part of the lead acetate paper is stained brown or black, the sample is viscose, while the absence of color indicates cuprammonium silk. They do not give any data upon the behavior of nitro or acetate silks under this test, but they were unable to obtain a positive test for carbon disulfide remaining in viscose.

### *Sulfuric-Acid Test*

Maschner[10] states that the rayons may be identified by placing 0.2 gram samples in small dry Erlenmeyer flasks standing on a white surface. Add about 10 cubic centimeters of chemically pure concentrated sulfuric acid simultaneously to each flask and shake gently to thoroughly wet the fibers. Note the immediate effect and continue the observation for about an hour and a half. Nitro silk is at first quite colorless but in 40 to 60 minutes the liquid assumes a weak yellowish tone. Cuprammonium silk immediately takes on a yellow to yellowish-brown tone and the liquid becomes yellowish-brown after 40 to 60 minutes. Viscose silk is at once turned reddish-brown by the acid and after 40 to 60 minutes the liquid is a rusty-brown color.

Clayton[2] reports that the concentrated sulfuric-acid test used to distinguish between viscose and cuprammonium rayons appears to be based partly on the assumption that the viscose gives hydrolysis products of a deeper color than those of cuprammonium. He claims that these tests cannot be regarded as conclusive, and that in carrying out the test it is important to give particular attention to any color change occurring in the first 15 to 30 seconds. The viscose becomes yellowish-brown, while the cuprammonium is colored a reddish-yellow. Tests for copper in the latter fiber are not always successful either, and he recommends a dyeing test as a check upon the results obtained by the other methods. On account of the greater hydration of the cuprammonium rayon, it is invariably dyed more deeply than viscose rayon when they are simultaneously placed in the same direct dye bath. He recommends Sun Yellow R in very dilute solution, in the presence of a little alkali, for this test.

*Ruthenium-Red Test*

Matthews[11] gives a very good account of the ruthenium-red test on various fibers. Ruthenium is one of the rare metals and most of its salts give an intensely red solution in water. This is especially true of the aqueous solution of the complex salt of ammonia with ruthenium oxychloride, $Ru_2(OH)_2Cl_4(NH_3)_7.3H_2O$. This reagent has been recommended for use in the microscopic examination of various fibers. While it is soluble in water, it is insoluble in both glycerol and alcohol. Ruthenium red is without action on fresh lignified tissue or that preserved in alcohol, but after the action of alkalies or sodium hypochlorite, the tissue is colored a bright rose. It colors the gums and pectin matters so widely found in vegetable fibers, as well as oxycellulose, but does not color pure cellulose, such as the clean normal cotton fiber. Raw unbleached cotton is quickly colored due to the presence of pectin or cuticle. Textile fibers containing pectocelluloses, such as linen, ramie, hemp and jute are strongly colored. Kapok is practically unstained, bleached wool is uncolored even after 12 hours and bleached true silk, which is at first not colored, becomes a rose color on standing. This reagent should be freshly prepared by dissolving 0.01 gram in 10 cubic centimeters of water. It is unstable in strong light.

Haerry[12] reports that ruthenium red is useful as a reagent for the identification of the rayons. Upon treating the rayon sample with the above reagent and allowing it to stand 12 hours, viscose becomes a distinct pink, more pronounced on standing. Denitrated Chardonnet (nitro) silk first becomes red but is more violet on standing. Cuprammonium silk is only slightly pink even after standing 12 hours; and acetate silk, which should remain uncolored, is sometimes irregularly tinted after 12 hours. This irregular tinting of acetate silk indicates irregularity in its composition and the test may have some value in detecting this fault. Rayon which has received the sthenose treatment is not colored.

### *The Iodine-Zinc Chloride Test*[f]

According to Schwalbe[6] it is possible to distinguish between viscose and cuprammonium silks by treating them with iodine-zinc chloride reagent, and washing with water. Both silks are at first colored, but whereas the viscose holds the bluish-green color for some time, the brown color of the cuprammonium silk soon washes out. Acetate silk is colored a distinct yellow by this reagent, and nitro a reddish-violet. This reagent is prepared by dissolving 20 grams of zinc chloride, 2 grams of potassium iodide, and 0.1 gram of iodine in 15 cubic centimeters of water. Maschner[10] reports that this test is not very satisfactory as different samples of viscose and cuprammonium silk react in different ways. Also see the zinc chloride-iodine test for mercerized cotton in Chapter VI.

### *The Iodine-Sulfuric Acid Test*[f]

The United States Bureau of Standards recently recommended a sulfuric acid-iodine solution, for the identification of rayons. This reagent, possibly giving about the same result as Hoehnel's iodine reagent, is freshly prepared for each test by dissolving 1 gram of potassium iodide in 25 cubic centimeters of water and adding iodine crystals to saturation. Pour off the clear solution and dilute this to about 25 to 50 per cent of its strength with water. Add an equal volume of 95 per cent sulfuric acid. When

[f] Where the fibers have been sized with a farinaceous product, any colorimetric identification test involving the use of iodine may give a misleading blue color.[22]

treated with this solution, viscose silk turns a blue color, acetate yellow, nitro violet, and cuprammonium a light blue. Haller and Ruperti[13] state that fully hydrolyzed Celanese gives a blue color with iodine in potassium iodide-sulfuric acid reagent, instead of the yellow obtained on ordinary Celanese. Gelatin silk, which is not a commercial product, is colored a yellowish-brown.

Clayton[2] recommends iodine solution as a quick method of identifying the various rayons. Celanese turns yellow to yellowish-brown when immersed in this solution, and the color is fairly fast to washing in water. Viscose and cuprammonium silks are colored a deep bluish-black by the same treatment but become very pale blue on continued washing. This test may be applied to the dyed Celanese fibers, provided the coloring is not too deep. Unfortunately wool and true silk are also colored yellow by iodine solutions but the burning test serves to distinguish these very readily by their nitrogenous odor. Another method of differentiating between true silk and wool on one hand and acetate silk on the other is to immediately place the yellow-colored fibers, after rinsing off the iodine solution, in a cold 1 per cent solution of caustic soda. The color of the true silk or wool is almost instantly discharged, while the color of the Celanese persists for some time. When using very fine filaments for this test, the strength of the caustic solution should be reduced.

When Celanese is partially hydrolyzed (saponified) by treatment with a cold, very dilute solution of caustic soda, it absorbs iodine from the solution with greater avidity than does the normal fiber. Even though the hydrolysis may be sufficient to allow staining of the fiber by direct dyes, the color of the iodine-stained fiber is only a light yellowish-brown after washing, which indicates a rather incomplete hydrolysis. However, when the acetate silk is boiled for a half a minute in a 1 per cent solution of caustic soda, it reacts towards the iodine solution in the same manner as the other rayons and mercerized cotton. This test may therefore serve as a quick, rough test for partially or unevenly hydrolyzed acetate silk.

### *Identification by Refractive Index*

The comparative low refractive index of acetate silk, which was mentioned as 1.474 to 1.479 in connection with its properties,

offers a very easy and simple method of identifying the undyed fiber either alone or in combinations with other fibers, under the microscope. It is well known that when a comparatively transparent colorless material is submerged in a liquid of approximately the same refractive index, it loses detail and under certain conditions is distinguishable only with difficulty. This principal may be used to identify, or rather to obliterate, the undyed acetate silk in a mixture of fibers.

If undyed acetate silk fibers, or materials containing it, are mounted on a microscopic slide in a medium of approximately the same refractive index as the fiber, the acetate fibers become practically invisible under the microscope. In fact in many instances there is enough visible change in the appearance of the fabric for an experienced worker to identify the acetate without putting it under the microscope. Through the microscope, only the fibers other than acetate are visible. When the fiber is dyed in light shades, this method is sometimes useful, but with heavy shades the color is so plainly apparent that the method is not often of value.

The refractive index of glycerol is 1.471 and that of lemon oil 1.473 to 1.476 at 25° C. W. Massot was possibly the first to suggest the use of glycerol in this manner, while Worden[14] suggested lemon oil for the same purpose. With Lustron and Celanese of the present type, lemon oil works very satisfactorily, while glycerol is a good substitute but is not quite so effective. The method is easy, quick and almost startling in its results to those who are not familiar with this phenomenon. In the above mediums, all other commercial fibers stand out clearly and distinctly, only the acetate silk disappearing.

Herzog[15] states that true silk may be identified and obliterated by a similar method. If a fiber of true silk is mounted in aniline, refractive index 1.599, and examined under a microscope with a Nicol prism, it is almost invisible when its longitudinal axis is at right angles to the plane of polarisation of the prism. It becomes more and more visible, when the stage is rotated, until it reaches a maximum of visibility at right angles to the original position. The older rayons have a refractive index between that of true silk

and acetate silk, and are therefore distinctly visible at all positions of the stage and prism.

Garner[18] suggests that acetate silk may readily be distinguished from the other rayons by the differences in their specific gravities and mentions an aqueous 40 per cent solution of potassium iodide, sp. gr. 1.4, as suitable for this purpose. In this solution, acetate silk, specific gravity about 1.3, floats, while viscose and cotton, specific gravity about 1.5, sink.

Another simple test for either white or dyed acetate silk is by means of the electroscope, and is based upon the fact that all vegetable fibers and rayons, with the exception of acetate silk, will remove the static charge from the electroscope, while acetate silk, true silk and wool do not dispel the static charge.

### *A. S. T. M. Tests*

Sub-Committee XV, of Committee D-13 of the American Society for Testing Materials, in a recent revised report of proposed rayon specifications have proposed the following as tests for the different rayon varieties:

Acetate: Twist fibers to tight wad and cautiously approach to match flame.

*a.* Acetate silks "melt" or "fuse" and burn more slowly than other rayons and harden at once into a light brittle substance, globular in appearance.

*b.* Viscose, nitro and cuprammonium silks all burn like cotton; that is, with no odor and leaving very little ash. Acetate silk is readily soluble in pure acetone to concentrations of not over 1 per cent. This serves as a confirmatory means of differentiating acetate silks from other rayons, which are not soluble in acetone.[g]

Nitro: Moisten the thread with a solution consisting of 1 per cent diphenylamine in concentrated sulfuric acid.

*a.* Nitro silks assume immediately a deep blue color. The fiber dissolves rapidly to a blue solution.

*b.* Viscose and cuprammonium silk are not colored blue and dissolve more slowly.

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[g] See footnote, page 71.

Cuprammonium: Immerse the thread for a minute in a boiling solution consisting of 1 per cent silver nitrate, 4 per cent sodium thiosulfate, and 4 per cent sodium hydroxide.[h]

*a.* Cuprammonium silk will remain unstained.

*b.* Viscose silk will be stained a brown or reddish-brown color. This reaction will also produce a brown stain on nitro silk.

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[h] In preparing this reagent, dissolve the silver nitrate and sodium thiosulfate separately. Add the first to the second and the cloudiness will disappear. Add the previously dissolved sodium hydroxide. Make up to correct volume, bring to boil, and filter.

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## TABLE XXI

### Reactions of the Rayons and Natural Silk

| *Reagent* | *Acetate* | *Nitro* | *Cuprammonium* | *Viscose* | *True Silk* |
|---|---|---|---|---|---|
| Burning | Melts, black residue | No odor, burns slower than viscose | Easiest to ignite, no odor, slight ash | No odor, burns slower than cuprammonium | Odor of burning feathers, black ash |
| Water | No swelling | All— | —Swell— | — | Very slight swelling |
| Acetone | Soluble | —All insoluble— | — | — | |
| Acetic acid | Soluble | —All insoluble— | — | — | Dissolves on boiling |
| Chloroform | Softens or dissolves | —All insoluble— | — | — | |
| Ammoniacal copper oxide | Swells but not dissolved | Swells quickly and dissolves slowly | Swells slowly and dissolves slowly | Swells and slowly dissolves | Fibroin dissolves |
| Chromic Acid | Swells but not dissolved | —Dissolves cold— | — | — | Dissolves slowly |
| Millon's Reagent | — | —Unstained— | — | — | Colored red |
| Decolorized Magenta | — | —Unstained— | — | — | Colored pink |
| Ammoniacal Nickel oxide | Swells but not dissolved | — | — | — | Dissolves quickly |
| Alkaline Glycerol Copper | — | —No change— | — | — | Dissolves quickly |
| *p*-Nitroaniline | — | —Uncolored— | — | — | Red |
| Diphenylamine | No color | Blue | No color— | — | |
| Brucine Sulfate | No color | Red | No color— | — | |
| Fehling's Soln. | Blue | Green | Blue | | |
| Alkaline Silver Nitrate | | | No change | Brown | |
| Sulfuric Acid | Slowly dissolves | Quickly dissolves, yellowish solution | Slowly dissolves, yellowish-brown solution | Quickly dissolves, rusty-brown solution | Quickly dissolves |
| Ruthenium Red | Colorless | Violet | Slight Pink | Pink | Rose |
| Iodine-Zinc Chloride | Yellow | Reddish-Violet | Brown | Bluish-Green | Pale Yellow |
| Iodine-Sulfuric Acid | Yellow | Violet | Light Blue | Blue | Yellow |

# CHAPTER VI

## THE DETECTION OF COTTON WHICH HAS RECEIVED THE MERCERIZATION TREATMENT AND ESTIMATION OF THE EXTENT OF THIS TREATMENT

WHILE mercerized cotton and other vegetable fibers do not belong in the rayon classification, their frequent presence in acetate silk combinations and the difference in their dyeing properties, as compared with both unmercerized cotton and the rayons, is sufficient justification for including the methods of detecting fibers which have received the mercerizing treatment. Practically all dyers are familiar with these differences in dyeing properties[1] but most of them are not so familiar with the methods of detecting and estimating the extent of this treatment.

Microscopic examination of the fiber or fabric has been and still is widely used as a method of detecting mercerized cotton, but the many widely different finishing treatments now given to all classes of fabrics, renders the microscopic method of detecting mercerized cotton more and more difficult and unreliable. Of course the differentiation of mercerized cotton and rayon under the microscope is very quick and accurate.

### *The Iodine Test*

One of the first successful chemical tests for the identification of mercerized fiber is that of Hubner[2] who gives a very complete and detailed account of his experiments. Hubner found that if cotton hanks which have been mercerized with sodium hydroxide solution of different strengths are immersed in a 0.01 normal iodine solution along with untreated cotton, at the moment of immersion a beautiful graduation of color is obtained, increasing in depth with the increase in strength of the soda solution used in mercerizing. After immersion for 5 minutes there is little difference in the depth of coloration between the unmercerized and that mercerized with 10° Tw. (1.05 sp. gr.) sodium hydroxide solu-

tion, while the hank treated with 20° Tw. (1.10 sp. gr.) solution is more colored than the 10° Tw.; the 22° Tw., stronger than the 20° Tw.; the 24° Tw., stronger than the 22°; the 26° Tw., much stronger than the 24°; the 28° and 30° Tw. each successively stronger than that proceding; the 40° Tw., much stronger than the 30° Tw.; the 45° Tw., stronger than the 40°; the 50° Tw., much stronger than the 45°, while the 60 and 70° Tw. (1.3 and 1.35 sp. gr. ) mercerized hanks are, if anything, rather lighter than the 50 Tw. (1.25 sp. gr.). Unmercerized hanks which have been steeped in this 0.01 normal iodine solution for 4 hours, after exposure to the air soon become white, while the mercerized samples show a color graduation depending upon the strength of the sodium hydroxide solution used, as mentioned above.

When the samples are immersed in 0.1 normal iodine solution and carefully washed in water, the typical brown coloration of both mercerized and ordinary cotton turns to a more chocolate shade. At a certain stage the ordinary cotton becomes rapidly decolorized, while the mercerized cotton turns a navy blue color, which, however, on repeated washings fades rapidly to white. With increased concentration of the iodine solution this blue coloration becomes more stable, and Hubner recommends a solution containing 20 grams of iodine in 100 cubic centimeters of a saturated aqueous solution of potassium iodide. The samples should be placed in this solution for a few seconds, when, after washing, ordinary cotton becomes a very light chocolate color, while the mercerized sample remains black. After further washings the untreated cotton becomes white, but the mercerized cotton remains a bluish-black color and fades only on prolonged washing.

Hubner also reports that mercerized cotton assumes a very dark reddish-navy-blue shade, while ordinary cotton is only very faintly tinged reddish by treatment with zinc-chloride-iodine reagent. He obtained the best results with the following reagent: Prepare a solution (*A*) containing 280 grams of zinc chloride in 300 cubic centimeters of water, and a second solution (*B*) containing 1 gram of iodine, 20 grams of potassium iodide and 100 cubic centimeters of water. To 20 cubic centimeters of *A*, add 4 drops of *B*, which corresponds to about 0.00195 gram of iodine. If the samples are

allowed to remain in the solution for 24 hours, the unmercerized cellulose is colorless while the mercerized cotton is a bluish-violet color. During this long exposure the iodine slowly disappears from the solution.

Kinkead[3] reports that the iodine test may be applied to flax yarns but that difficulty is encountered in applying it to linen cloths on account of the necessity for the complete removal of all traces of starch. A very slight trace of starch will give a deep blue color which entirely masks the reaction.

### *The Benzopurpurin Test*

The late Prof. Knecht[4] pointed out the remarkable difference in the behavior of ordinary and mercerized cotton dyed with Benzopurpurin 4B on treatment with hydrochloric acid. Ordinary cotton dyed in this manner is at once turned blue by the hydrochloric acid but mercerized cotton assumes a reddish-violet color, provided not too much acid is used.

If the acid solution containing the dyed cotton sample is heated, and a dilute solution of titanous chloride slowly added, the color of both samples gradually diminishes in intensity, until, just before the complete decolorization, the ordinary cotton appears indigo-blue and the mercerized cotton red. This distinction is only visible in case the mercerized sample has been treated with caustic soda solution of over 30° Tw. (1.150 sp. gr.) strength, unstretched, or 35° Tw. (1.175 sp. gr.) under tension. Further experiments by Knecht indicate that the amount of dyestuff (Benzopupurin 4B) taken up by cotton upon treatment for an hour in a 20 to 1 dye bath containing 3 per cent of dyestuff, 5 per cent of sodium carbonate and 10 per cent of salt, varies gradually from ordinary cotton with increasing strength of the caustic solution, up to 70° Tw. (1.350 sp. gr.) caustic solution.

Knaggs[5] proposes a simpler modification of Knecht's Benzopurpurin-titanous chloride test, and states that if samples of ordinary and mercerized cotton are dyed with a trace of the dyestuff, with or without a little salt, on dropping acid into the boiling dye bath until the ordinary cotton has become blue-black, the mercerized cotton will appear red. He proposes to make this test by using a dye bath containing 5 cubic centimeters of a solution con-

taining 0.1 gram of Benzopurpurin 4B, in 100 cubic centimeters of water, with or without a little salt, and dropping in about 2 cubic centimeters of strong (34.5° Tw.) hydrochloric acid. He also states that while Congo Red GR gives the same test, Congo Red 4R is not very sensitive to acid, and discusses the theory as advanced by Knecht.

Kinkead[3] points out the difficulties encountered in applying the Benzopurpurin test and says that it "does not command confidence in general, because different materials require different quantities of acid to render the distinction evident. It appears impossible to find an acid solution of such strength that it could be used as a general reagent. For instance, an acid solution which gives the reaction with a heavy closely woven damask in a satisfactory manner, is much too strong when testing an open woven cloth or a small cutting of yarn. Such a strong solution, with these open weave materials, would turn both the mercerized and unmercerized samples a blue color, while if the acid solution is only sufficiently strong to turn the color of the open-weave unmercerized cloth red, then both samples of the heavy damask remain entirely unchanged when treated with this solution. Moreover, the depth of shade produced on the material by the Benzopurpurin is also a controlling factor, the deeper the color of the cloth, the stronger is the acid solution required to give the reaction. This method therefore cannot be considered satisfactory, as in the absence of a similar piece of material known to be unmercerized, it does not give a definite indication."

### *The Kinkead Test*

Kinkead[3] gives one of the latest and probably most reliable methods of determining whether vegetable fibers, including cotton, linen, ramie and hemp, have received treatment with strong sodium hydroxide solution, as in mercerizing. A small sample of the desired material is stained by soaking it for a few minutes in a 0.001 per cent aqueous solution of Methylene Blue (preferably zinc-free hydrochloride), containing 0.5 per cent of sodium carbonate. The stained material is rinsed with distilled water and in the case of cotton, ramie or hemp, covered in a test tube with about

10 cubic centimeters of a 1 per cent sodium carbonate solution. In testing linen a 3 per cent carbonate solution is used in place of 1 per cent. Four drops of iodine solution are then added. This iodine solution is prepared by dissolving 1 gram of iodine in 100 cubic centimeters of 20 per cent aqueous potassium idodide solution. The test solution is rapidly heated to the boiling point, poured off, and immediately replaced by fresh cold sodium carbonate solution of the same strength as above; i.e., 1 per cent for cotton or 3 per cent for linen. Under this treatment the coloration of the mercerized material becomes reddish-purple, that of unmercerized material remaining blue, often with a greenish shade. If an unmistakable purple color is not obtained, it may be concluded that the material has not been mercerized by a normal process.

In making the test, prolonged heating of the stained goods in the carbonate solution should be avoided as this removes considerable color from the sample. In many cases, it will be seen that the color change occurs on very slight warming, and when a qualitative test only is required, this may be taken as sufficient evidence of mercerization. It is desirable to pour off the first carbonate solution as it contains some color due to stripping, which may tend to mask the color change. It also quickly cools the test piece, which is desirable. When the hot solution is allowed to act for about a minute, it may cause a slight color change, towards the purple, on unmercerized goods, but the addition of a cold soda solution restores the original blue color. In the same manner, a lightly mercerized sample may assume quite a reddish-purple color when hot, but becomes much bluer as the solution cools.

The second solution should never be heated as almost any alkaline solution, however weak, will produce the color change on unmercerized material if allowed to act for sufficient time at a high temperature. The shade of the unmercerized material is quite unaltered by the carbonate solution under the conditions of the test. Even after remaining in the cold carbonate solution for 3 or 4 hours, the shade of the unmercerized material will be only slightly changed. The difference between the colors of mercerized and unmercerized material is quite distinct after remaining

in the carbonate solution for 3 days. Table XXII gives the colors obtained on materials mercerized under various conditions. An important factor in this test is that acid treatment or bleaching after mercerizing, even if drastic, does not appear to affect the result of the tests.

TABLE XXII

COLOR OF MERCERIZED CELLULOSE WITH KINKEAD TEST[3]

| Strength of NaOH °Tw. | Sp. Gr. | Color Change |
|---|---|---|
| 0.0 | 1.000 | Bright blue, no change. |
| 20. | 1.100 | Only very slightly redder. |
| 30. | 1.150 | Definitely redder. |
| 40. and 50. | 1.200 to 1.250 | Full purple and definitely the reddest of the series. |
| 60. and 70. | 1.300 to 1.350 | Rather bluer than 40° and 50°. |

### *Sulfuric Acid-Formaldehyde Test*

Mennell[6] states that mercerized cotton is more readily attacked by sulfuric acid than normal cotton, and that while 1.375 sp. gr. sulfuric acid has practically no action on normal cotton, mercerized cotton is appreciably affected. The action of 1.600 sp. gr. sulfuric acid diluted to 1.375 with 40 per cent formaldehyde solution, is even greater than that of the sulfuric acid of this strength alone. This latter reagent may be prepared by diluting 320 cubic centimeters of 1.600 sp. gr. sulfuric acid with 260 cubic centimeters of 40 per cent formaldehyde solution. The mixture is about 1.375 sp. gr. The sample to be tested, together with standard samples of both normal and mercerized cotton, is treated in this reagent for 2 minutes at room temperature. They are then well washed and neutralized with hot dilute sodium carbonate solution.

The effect of the sulfuric acid-formaldehyde reagent on the samples is very clearly shown on dyeing them with most substantive dyes, but Chlorazol Sky Blue GW is suggested as particularly suitable for this purpose. The samples should all be dyed together in a slightly alkaline (with sodium carbonate) very dilute boiling dye bath. The amount of dyestuff to be used may be determined by experiment but usually by using a dye bath which gives a 0.1 per cent shade, on the weight of the cotton, on the normal or

unmercerized sample, a well mercerized sample will be colored equivalent to about a 0.8 per cent dyeing.

Before testing dyed samples, the color should be stripped with sodium hypochlorite or hot alkaline hydrosulfite. The stripping operation does not affect the test in any way. The acid-formaldehyde reagent keeps well and the formation of a para-formaldehyde sediment does not interfere if it is mixed well before using. The colors obtained are permanent, which is an advantage over the Hubner test and by comparing the colors obtained on the various samples, it is possible to estimate the degree of mercerization.

### *Haller's Method*

Haller[7] estimates the degree of mercerization of cotton samples by dyeing them together with standard mercerized samples and then comparing the amounts of white, black, and pure color tone in the dyed samples in the Ostwald chromometer. He states that while the method is rapid it is somewhat less accurate than the titanous chloride method of Knecht. Examination of the color contents of cotton fabrics with sodium hydroxide of 2 to 30° Be. (1.014 to 1.261 sp. gr.) and afterwards dyed with Diamine Blue 3R, Benzo Azurine, and Congo Red, shows that the black and white constants of the resulting shades remain constant from 2 to 12° Be. (1.014 to 1.091 sp. gr.), then distinctly increase and decrease respectively from 12 to 26° Be. (1.091 to 1.221 sp. gr.), and then remain constant. Simultaneously the content of pure color decreases similarly but less regularly. It is concluded that the chief mercerization effects are produced by sodium hydroxide of 12 to 26° Be., although Knecht found that the mercerizing action distinctly starts with a 7° Be. (1.052 sp. gr.) solution.

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# CHAPTER VII

## DYEING THE OLDER RAYONS

### *Nitro, Viscose and Cuprammonium Silk*

Now that we have a better understanding of the constitution and properties of acetate silk and the points wherein it differs from the older rayons, it may be well to briefly review the methods of dyeing the older rayons; i.e., nitro, viscose and cuprammonium, so as to bring out even more clearly the differences in the dyeing properties of acetate silk and those of all other cellulose fibers. As the dyeing of these older rayons is so well understood by everyone in the industry, it is useless to go into detail here.

In general the behavior of the older rayons to dyestuffs is similar to that of cotton,[1] with this difference, that the older rayons, consisting of hydrocellulose, have a greater affinity for most dyes than has cotton cellulose. It naturally follows that in these cases for equal weights of the two substances, the rayon requires less dyestuff than the cotton. All varieties of rayon have an affinity for the basic dyes but some varieties have far more affinity for them than others, and as usual, the affinity of the different members of the basic class of dyes for each type of rayon varies somewhat from that of the other members of the same classification.

As has previously been mentioned, Lustron acetate silk has a greater affinity for the strongly basic dyes than any other textile fiber. The affinity of Celanese acetate silk for certain basic dyes follows that of Lustron.[2] The affinity of nitro, viscose and cuprammonium silks for the basic dyes decreases in the order named. While acetate silk has no affinity for most of the direct cotton and sulfur dyes, these may be used on all of the older rayons. Certain vat dyes, under some conditions, have an affinity for acetate silk, but practically all of them are used upon the older rayons for very fast shades.

*Dyeing Nitro Rayon*

Nitro silk is also known as Chardonnet, nitrocellulose, collodion, pyroxylin, du Vivier, Frankfurter, soie de France, Meteor, Strehlenert, Besancon, Hungarian, Tubize, and Lehner artificial silk. Nitro silk, as the variety of names indicate, is manufactured in many different plants and while all are similar in appearance, in most instances the product of each plant differs in some slight degree from that of the other plants. Nitro silk is usually more lustrous than natural silk, harsher and without the characteristic feel of true silk. It has been stated that the original undenitrated Chardonnet silk more closely approaches the present acetate silks in many of their desirable properties, than any other type of rayon.

Nitro silk has a great affinity for the basic dyes, whereas viscose and cuprammonium are best dyed by substantive dyes. Nitro silk is dyed even to deep shades by the basic dyes without mordanting, probably due to its combined oxycellulose and hydrocellulose content, but viscose and cuprammonium silks should first be mordanted with tannin and tartar emetic before applying the basic dyes. The fastness of the basic dyes on nitro silk to washing is increased by top-mordanting them with tannin and antimony in the usual manner. On account of the high affinity of nitro silk for the strongly basic dyes, acetic acid is frequently used as a retard and to aid leveling in applying them to this fiber. The weakly basic dyes show much less affinity for nitro and therefore must be applied in short baths of high concentrations, or on a mordant, to give deep shades.

In general, nitro silk has less affinity for the direct cotton dyes, as a class, than either viscose or cuprammonium. In fact, it has been stated that the affinity of the direct cotton dyes for all of the rayons, acetate included, is just the reverse of the affinity of the basic dyes as given above. However, the direct dyes are frequently used on nitro silk, especially for light and medium shades. The vat and sulfur dyes may also be used on nitro silk but in applying the sulfur dyes, care must be taken to avoid loss of luster and strength.

*Dyeing Viscose Silk*

Viscose silk is also known as vistra, staple fiber, xanthate, Luna, Stettiner, Du Pont and Celta[a] silk, and is prepared from solutions of mercerized cellulose in caustic soda and carbon disulfide. It is a regenerated cellulose with a fine glossy appearance. Its affinity for dyestuffs is similar to that of mercerized cotton and it appears to have an intermediary affinity, for both the basic and direct cotton dyes, between nitro and cuprammonium silks. In other words, it has more affinity than nitro silk for the weakly basic dyes, but less affinity than the cuprammonium. Basic dyes may be used for pale and medium shades without a mordant, but for heavy shades it should be mordanted and dyed in the presence of acetic acid.

Wilson and Imison[3] found that the affinity of viscose silk for the direct cotton dyes varies not only with the method of manufacturing the rayon, but also with the molecular complexity of the dyestuff used. They point out that in a general way, the inequality of different lots of viscose is less evident in applying direct cotton dyes of low molecular weight, than with those of higher molecular weight. They give a list of dyes showing their comparative leveling powers. Further, dyeing at high temperatures is more likely to yield level shades than similar dyeing at lower temperatures.

Hall[4] points out that in order to obtain the best results with the direct dyes on viscose the following points should be considered:

1. The higher the temperature of the dye bath, the more level the shade.
2. In using direct dyes which have an affinity for viscose, the best results are obtained by the use of only soap in the dye bath.
3. The use of sodium sulfate or chloride in the direct dye bath on viscose tends to produce uneven shades and their use should be reduced to the minimum.

[a]Celta is a Swiss macaroni or hollow, soft, rough surfaced rayon with less than the usual luster. Sniafil artificial wool is a variety of viscose which has received a special finishing treatment. Most of the so-called "artificial wools" are also prepared from viscose.

4. In dyeing compound shades, dyestuffs having approximately the same leveling powers should be used as far as possible, as it is unwise to mix even dyeing products with those known to dye unevenly.

On viscose the sulfur dyes frequently give uneven results and their use should for this reason be avoided unless the fastness requirements demand their use. Of course, this unevenness is not so noticeable in heavy shades as on the tints, and, therefore, in applying the Sulfur Blacks this trouble is less prevalent. While vat dyes are coming into more extensive use on viscose, most of it is at present dyed direct. As is the case with all other dyes, certain vat dyes are far more level dyeing[4] on the older rayons than are other members of the same class.

### *Dyeing Cuprammonium Silk*

Cuprammonium silk, known also as glanzstoff, cupra, cuprate, cellulose cuprate, copper ammonium, copper, Despaisis, Eagle, Julich, Givet, Crinol, Elberfeld, Aachen, Langhaus, Fremery, Oberbrucher, Sirius, Aix la Chapella, Bemberg, Thiele, Pauly, and Parisian silk, is made by the ammonium copper oxide process and the different products are all similar in appearance and properties. It has a very high luster, in some cases surpassing that of nitro silk, and its feel approaches that of true silk. Cuprammonium silk has less affinity for the basic dyes than either nitro or viscose silk, and for full shades the cuprammonium silk should be tannin mordanted. It has the highest affinity of any of the rayons for the direct cotton dyes, which give excellent results on this fiber. Sulfur and vat dyes are also used but care must be taken to avoid loss of luster. This rayon has a higher affinity for the weakly basic dyes than for those of strongly basic characteristics, which is exactly the reverse of the case with nitro silk. In applying the weakly basic dyes to tannin mordanted cuprammonium silk, 5 to 10 per cent of acetic acid may be used in the dye bath, adding the dye to the bath gradually and raising the temperature slowly to avoid unevenness, to as high as 70° C. (156° F.)

### *General Dyeing Formulas for Rayons Other Than Acetate*

While it has been suggested to apply the direct dyes to viscose and cuprammonium at a temperature as low as 40° C. (104° F.), without doubt better penetration and more level results are obtained at higher temperatures. For instance, The Ciba Company recommend that their Chlorantine Fast dyes be applied to viscose from a 20 or 30 to 1 neutral salt bath containing 10 to 20 grams of sodium sulfate per liter of dye bath, entering the goods at 32° C. (90° F.) and completing the dyeing within an hour at 60 to 80° C. (140 to 175° F.). In dyeing light shades, and as an aid in leveling and penetrating, soap or Monopole oil and/or sodium borate, phosphate, or carbonate may be added to the dye bath.

Some acid dyes are also used but they are not usually fast to washing and the basic dyes have such a high affinity for some varieties of the fiber that in some instances it is almost impossible to secure level shades. The basic dyes are usually applied at temperatures up to 40° C. (105° F.) to the previously wet-out rayon with 2 to 10 per cent of acetic acid. For heavy shades and colors of better fastness to washing with the basic dyes, a tannin and tartar emetic mordant should be applied in the same manner as on cotton.

### *Mordanting Rayon*

In mordanting either viscose or cuprammonium silks for the basic dyes, the rayon should remain for 2 or 3 hours in a bath containing 2 to 5 per cent of tannin and 1 per cent of hydrochloric acid, on the weight of the goods, at 50° C. (122° F.). The material is then removed, the excess of liquor removed (but not rinsed), and treated for about 20 minutes in a fresh cold bath containing 1 to 2.5 per cent, or about half of the percentage of tannin used, of tartar emetic. Hall[4] states that more even shades are obtained on viscose mordanted with Katanol than on tannin-antimony mordanted viscose, and gives a table to support this statement. If particularly fast dyeings are wanted, such as for cross-dyeing, the basic dyes should also have a top mordant by repeating the above process after dyeing. Basic dyes are often used to top the substantive dyes on rayons, thus brightening the shade.

When the sulfur dyes are used on the rayons they are usually applied from a 25 to 1 dye bath containing the same quantity of sodium sulfide as dyestuff, 1 to 4 per cent of sodium carbonate and 5 to 25 per cent of sodium sulfate, dyeing at 38 to 49° C. (100 to 120°F.) for about an hour. Copper vessels must not be used. The vat dyes are now coming into more general use on the older rayons and are applied in the usual alkaline hydrosulfite vat. In general they have less affinity for nitro than for the viscose and cuprammonium silk.

Really good deep blacks on rayon, such as on hoisery, are usually obtained by first applying dyes of the Diazo Black type, diazotizing with sodium nitrate and hydrochloric acid, and then developing with *B*-naphthol or phenylenediamine, in the same manner as in dyeing cotton. Brown shades of good fastness to washing and cross dyeing may be obtained with Primuline and a Diazo Black, diazotized and developed with resorcinol or phenylenediamine. Brown shades of good fastness to light may be obtained with sulfur dyes.

The fact that acetate silk cannot be dyed fast shades by any of the foregoing methods greatly hindered its use in the textile industry except for white stripe effects, etc., and where color fastness requirements were not rigid, until the discovery of the special acetate silk dyes.

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# CHAPTER VIII

## THE DYEING PROPERTIES OF ACETATE SILK AND THE HYPOTHESES ADVANCED TO EXPLAIN THE PHENOMENON

FROM our knowledge of the difference in the chemical constitution of acetate silk, as compared with that of the older rayons and natural textile fibers, which in the case of the rayons may very well be compared to the difference in constitution between olive oil and glycerine, we would certainly expect some difference in properties. However, when we come to consider the dyeing properties of acetate silk, we may even be surprised to find them so entirely different from those of the parent compound, cellulose, or the related rayons.

Briefly, acetate silk has dyeing properties peculiar to itself and entirely different from those of any other commercial textile fiber. One of the chief drawbacks in the early attempts to dye it was due to the fact that everyone wanted to use the known common dyes upon it by the older ordinary methods of application. We cannot successfully dye cotton with acid wool dyes, nor wool with substantive dyes, as a class. Therefore, as a new class of fiber, we may expect really satisfactory results only from a new class of dyes, developed especially for this new fiber, just the same as we have certain other classes of dyes for the older known fibers of different constitution and properties.

Most textiles depend upon their color for much of their attractiveness, and therefore a fiber or fabric which may readily be dyed is in much greater demand than another fiber with the same textile, physical, and chemical properties, but which cannot be dyed in fast, brilliant, and attractive colors. There is no doubt whatsoever that, during its early history, acetate silk was greatly handicapped by its dyeing properties, or rather lack of them, in connection with the only dyestuffs then in use. While there is a certain definite demand for fibers which are not dyed or stained in the

ordinary dye bath, the actual consumption of fibers for this purpose, in pounds, is comparatively small for use as white effects only. Possibly the present wide interest in acetate silk is at least in part due to the attractiveness and fastness properties of the dyed fiber, and the ease of application of these fast colors by means of the new dyes developed particularly for this fiber.

*History of Acetate Silk Dyeing as Compared with Cotton Dyeing*

It is not difficult to recall that at one time in the history of cotton dyeing, the dyeing of cotton was in practically the same status as the dyeing of acetate silk in its early days or rather years. Today we are so familiar with the use of the direct cotton, vat, and other dyes that we are a little prone to forget some of the difficulties of former times. Before the discovery of the direct cotton dyes, the fast dyeing of cotton was possibly in an even worse state than was the dyeing of acetate silk before the discovery of the first special acetate silk dyes, the Ionamines.

However, the chemists of today are much better equipped to combat a situation such as at one time existed in connection with cotton, and we have a much wider range of more or less suitable dyes for experimental purposes. But even so, before the discovery of the Ionamines in 1922, there was no special class of dyestuffs for acetate silk, no one class of dyestuffs which would give reasonably fast shades in all colors, and which could be used in wide combinations with other dyes on unions, etc. While certain commercial dyes and other compounds were applied to acetate silk with more or less success, probably only a few of these were wholly satisfactory for the purpose intended.

From the early literature and patents upon the dyeing of acetate silk, it appears that the early acetate silks which presumably all consisted of primary cellulose acetates, were particularly refractory in dyeing. With the advent of the later secondary acetates, more progress was made in the dyeing. Whether this was due to the change in the products themselves, or the accumulated knowledge and experience, is not clear. Very possibly both factors played a part, with the change in properties of the newer fiber in the leading role. A large part of the early dyeing troubles appear

to have been due to the extreme difficulty in even thorough wettingout the fiber, on account of the high interfacial surface tension in all aqueous solutions, dye baths included.

As would be expected, the difficulties in applying the older and then well-known dyes to acetate silk first resulted in a search for new and better methods of applying them to this new fiber. One of the first of these methods to be developed was by means of "swelling" agents, such as alcohol or other organic solvents in the dye bath. This led to the use of mineral acids in the bath, which caused a hydrolysis of the cellulose acetate, probably resulting in a product somewhat resembling the cellulose acetate produced by the Miles patent. This in turn appears to lead up to Mork's saponification process of dyeing.

The fact that all other textile fibers, including all of the other rayons, are turgoids, and as such swell in water or aqueous solutions, might lead us to expect good results by the swelling processes of dyeing acetate silk. In practice this process was never very successful on acetate silk. It was expensive, impractical, and unsatisfactory, and is no longer used in dyeing. The saponification process permitted acetate silk to be dyed by the products commonly used in cotton and the older rayons, but it, too, is no longer used, except on special cases, such as in printing. However, it was a distinct advance in the art and was probably more satisfactory on the older primary acetate than the later secondary acetate silks. The early difficulties in dyeing acetate silk not only led to research upon new dyeing methods and special dyes, but also resulted in several attempts to manufacture a colored acetate silk fiber. This particular development was discussed in Chapter III.

The numerous difficulties encountered in dyeing acetate silk with the older, common, and better-known dyestuffs, even by the special methods, led to a great deal of research work and considerable study upon the subject of special acetate silk dyes by some of the most brilliant dye chemists in the world. As Celanese is the product of English research since the war, and the English manufacturers in general appear to realize the value of chemical research in all lines, it is not surprising that practically all of the most recent and valuable advances in this field have been made in

England. In the production of these new dye products, the members of the research staffs of the British Dyestuffs Corporation, the Scottish Dyes, Ltd., and the British Celanese, Ltd., stand foremost as pioneers. In applying the results of this research, it should be remembered that possibly all of the work was done upon Celanese. While most of the results are also applicable to Lustron and Rhodiaseta as well as other varieties of acetate silk, there may be some minor variations or exceptions in certain instances.

### *The Solution Theory of Dyeing*

As a result of the discovery of these new dyes and dyeing methods, a number of hypotheses have been advanced to explain just why certain products or classes of compounds are applicable, while others are not. As might be expected, all of this research and discussion has had a certain influence and value in connection with the dyeing of, and dyes for, all other fibers. At the present time the solution theory of dyeing acetate silk appears to receive the most support, but it is very probable that no one theory will satisfactorily explain the dyeing of any one fiber by all dyes, and that acetate silk is no exception in this respect.

While the solution theory of dyeing acetate silk appears to favor the mechanical theory of all dyeing, it does not necessarily prove it. In truth, the very fact that acetate silk is not dyed by the direct cotton and other dyes of the acid type has been used to assist the proof of the chemical theory of dyeing cellulose. Undoubtedly more than one factor enters into the dyeing of acetate silk, just as it does into dyeing all other textile fibers. The high affinity of the color base of basic dyes and of compounds containing the strongly basic amino group, as well as many other basic compounds, for acetate silk, which is certainly of an acidic character, most certainly indicates that chemical factors play some, and possibly, the most important part.

The fact that dyes which are soluble in ethyl acetate as a rule dye acetate silk does not prove that dyeing acetate silk is a solution phenomenon. There is nothing to prevent the formation of compounds between the base of the dye and the acidic radicle of

the solvent (ethyl acetate) in at least some of the cases. Without doubt where the solubility of the dyestuff in the fiber is greater than its (dyestuff) solubility in water, this solubility factor plays the important part in dyeing, but unless some form of chemical change or combination takes place, we would hardly expect these dyes applied by solubility alone to be fast to washing. In the case of the dispersol dyes, the method of solubilizing or dispersing the comparatively insoluble dyestuff is an important factor in its application and fastness, but this hardly explains the fastness of the strongly basic dyes on Lustron, the most acidic textile fiber of commerce.

If dyeing acetate silk is entirely a solution phenomenon, why is it that very few compounds except those of a basic[a] character, or containing strongly basic groups, are soluble in acetate silk? A great many investigators appear to fear a chemical theory of dyeing any fiber, wool and silk included. They may look farther and do worse than a chemical theory in many instances. The following is a very brief discussion of some of the recent papers upon the hypotheses advanced to cover acetate silk dyeing.

*Hypotheses*

Knoevenagel[1] was possibly the first to suggest the solution theory of dyeing acetate silk. He explained the absorption of phenols and amines by this fiber as a sort of "solid solution" in which the chemical and fiber took part. Possibly Knoevenagel's discovery[b] of the fixation of the amines and phenols by acetate silk forms the basis of our present acetate silk dyes,[2] especially the Ionamines and other developed dyes.

Green and Saunders,[3] in discussing the Ionamines, appear to favor the solution theory to some extent and compare the dyeing of acetate silk with that of hydrocarbon oils, such as paraffin or benzene, and mention the Sudan dyes, which color both acetate silk and hydrocarbon oils. They also state that benzene will remove a certain amount of some colors from acetate silk and give an interesting experiment with Ionamine A in an aqueous-benzene mixture.

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[a] Also see Ellis, page 281.
[b] See German Patent No. 198.008.

On shaking an aqueous solution of Ionamine A with cold benzene, the water is yellow and the benzene colorless, but upon warming and then shaking, the benzene eventually becomes yellow and the water nearly colorless. They explain this by pointing out that in the aqueous solution the aryl-omega-sulfonate is in equilibrium with the base-aldehyde-bisulfite, the balance being greatly in favor of the omega-sulfonate. In the presence of benzene, this balance is disturbed by the base passing into solution in the benzene. Acetate silk resembles benzene in that it absorbs little water when wetted. Also the interface, like that of benzene-water, acts as a semipermeable membrane, permitting the passage of the base but not of the aldehyde-bisulfite.

The hydrolysis of the dye compound is thus greatly increased, since the basic compound is continually removed by solution in the non-aqueous solvent (acetate silk or benzene) while the semipermeable character of the interface prevents the passage of aldehyde-bisulfite, to establish an equilibrium in the non-aqueous phase. Once within the acetate silk, the bases are firmly held (chemically?) as are most amino compounds, and hence show excellent fastness to soaping, washing, perspiration, etc. In the case of wool, which has a basic character and absorbs water, the unhydrolyzed Ionamine is probably taken up by the protein in the same manner as an acid dyestuff. This would tend to retard the hydrolysis of the Ionamine.

Hall[4] points out that substances which form stable or water soluble salts, either with alkalis or acids, as for instance *o*-hydroxybenzilideneacetone or aniline, are absorbed by the acetate silk but are largely removed by washing, and that the size and complexity of the dye molecule play a part in dyeing acetate silk. He writes that in a general way, the lower the molecular weight or the simpler the structure of the dyestuff, the more readily it dyes acetate silk and the more strongly it is retained. For instance, with Magenta ($C_{20}H_{20}N_3Cl$) which has a relatively high molecular weight, there is some difficulty in obtaining deep fast shades on Celanese. However more recent[11] work does not appear to support his views regarding the importance of the molecular simplicity, as some of the products giving fast heavy shades by the

dispersol method have a heavy, complex molecule, similar to that of the vat dyes.

Meyer, Schuster and Bulow[15] state that the dyeing of undenitrated nitro silk (cellulose nitrate) proceeds by solution of the dyestuff in the fiber in the same manner as in dyeing acetate silk and that the same dyestuffs may be used. They found nitroaniline to be over a hundred times more soluble in this fiber than in water.

In any discussion of the theory of dyeing acetate silk, the role of the sulfonic acid groups in dyestuffs must not be overlooked. As is well known, the sulfonic acid group is widely used in connection with certain classes of organic compounds, particularly acid dyestuffs, to confer solubility in water. While it is certainly a very great help in solubilizing these compounds in water, it does not increase their solubility in organic solvents, such as benzene or ethyl acetate, and in fact usually reduces it considerably. This fact also holds good with acetate silk and appears to play an important part in any attempt to apply the sulfonated dyes to this fiber. This may appear to support the solution theory of dyeing; however, the strongly acidic character of the sulfonic group, in conjunction with the acid character of acetate silk, may have some significance to those who look for a chemical theory. As might be expected, in the case of acetate silk the adverse influence of the sulfonic group may be overcome to some extent by the presence of certain other groups, usually of a basic character.

Carboxylic acid groups also have the property of solubilizing certain relatively insoluble organic compounds in water, but does not reduce their solubility in organic solvents, as in the case of the sulfonic groups. For this reason the carboxyl group has been used in place of the sulfonic group, to solubilize certain dyes for acetate silk with considerable success. Here again the less acid character of the carboxyl group may serve to explain a point in the chemical theory of dyeing acetate silk. Nitro groups may also be present in acetate silk dyes without detrimental effects.

The stability of the sulfonated dyes may also play a part in their lack of dyeing affinity for acetate silk. Greenhalgh[5] points out that in some instances the staining of acetate silk by acid and

direct cotton dyestuffs is due to a selective absorption of the base of the dyestuff by the acetate silk. He states that in some instances the affinity of the acetate silk for the base is sufficient to cause the withdrawal of the base from the dyestuff molecular complex, thereby giving a partial decomposition of the dyestuff. This certainly does not entirely support the solubility theory of dyeing acetate silk only. While the acetate radicle of the fiber may be able to withdraw the basic group from certain dyestuffs under some conditions, we would hardly expect it to be able to overcome the affinity of the strongly acid sulfonic group for the dyestuff base in every instance. It is interesting to note that Prof. Hibbert states that the basic dyes are possibly attached only to the acetate groups in acetate silk.

Greenhalgh also points out that the dyeing of acetate silk by the commercial magenta dyestuff is due entirely to the absorption of the magenta base, and not of the salt of the base. Very probably this statement holds true for many of the basic dyes. The fact that they are retarded in the dye bath by the presence of either acetic acid or sodium chloride, both of which would tend to diminish the amount of free color base in the dye bath, indicates that this statement is correct. The dyeing of acetate silk by means of bases in colloidal solution (dispersol method) also supports this statement.

According to Caille[6,16] the affinity of the basic dyes for the cellulose esters (acetate and nitrate) appears to be largely dependent upon the amount of combined sulfuric acid present in the ester. He gives tables showing that the percentage of basic dyestuff fixed by the cellulose derivatives varies with the percentage of combined sulfuric acid, but this variation is not proportional, and in the case of cellulose acetate, the combined acetic acid plays a secondary part in the fixation of the basic dyestuff. With dyestuffs such as Methylene Blue and Auramine on acetate silk, the combined sulfuric acid is the main factor, even where the acid has been neutralized with calcium. He believes that the oxycellulose present with the cellulose esters in the fiber also influences the basic dyestuff affinity, but to a considerably smaller extent than the combined sulfate radicles. Even in denitrated

nitro silk the sulfate esters play a very important part. Yet Caille does not believe that the dyeing of the cellulose esters is a chemical phenomenon, mainly for the reason that the amount of dyestuff fixed by the ester is not proportional to the total sulfuric acid content.[c]

### *Surface Fixation of Dyestuffs*

Paneth and Radu[7] report that while cuprammonium and nitro silks are stained throughout, even when the absorption of basic dye has not attained its maximum, sections show that acetate silk is stained only externally by Methylene Blue. Their experiments upon one particular variety of acetate silk, probably Celanese, shows the absorption of Methylene Blue on this fiber to be of the same order as that by the diamond. In other words it is entirely as a monomolecular layer and may be used as a method to measure the surface area of the acetate silk. Ginsberg[8] states that it took almost four months to completely dye an acetate silk, variety not stated, with Methylene Blue.

Meyer, Schuster and Bulow[2], and Meyer[9] confirm this work regarding the surface fixation of certain basic dyes on acetate silk in the form of a monomolecular layer and explain it on the basis of Langmuir's explanation of the layer of soap on water. Langmuir shows how the water-soluble groups of the soap-fatty acid molecule, *i.e.*, the carboxyl group, actually penetrates the water. In the same manner they explain that the aromatic portion of the basic dyestuff is soluble in acetate silk, while the salt-like group, such as ammonium hydrochloride, which is itself soluble in water, does not penetrate the fiber. If Langmuir's theory is correct in the case of soap and water, and it very probably is, very possibly the same explanation may hold good to some extent for the application of certain basic dyes to acetate silk.

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[c] From a study of the known properties, composition, etc., of Lustron and Celanese, it appears probable that Lustron may consist of the primary cellulose acetate while Celanese consists of secondary acetate. The dyeing and non-blinding properties of the former (Lustron) suggest that it may also contain some neutralized sulfuric acid groups. This may account for its high affinity for the basic dyestuffs, in which it surpasses all other textile fibers. Celanese, on the other hand, contains some hydroxy groups, similar to those present in the regenerated cellulose rayons, which accounts to a large extent for the differences in the dyeing properties of the two ester fibers.

*Dyeing With "Assistants"*

In applying basic dyes with "assistants,"[d] the aromatic portion of the basic dye unites with the mordant or assistant to form a compound which is more soluble in, or has more affinity for, the acetate silk than the complete dyestuff alone. This is indicated by shaking an aqueous solution of a basic dyestuff with ethyl acetate, when, upon the addition of the assistant, the ester is deeply colored. While the dye-assistant compound enters and dyes the interior of the fiber, the surface action probably also takes place simultaneously to some extent, the process of solution and absorption occurring one upon the other, to give deep shades of increased fastness.

Meyer, Schuster and Bulow[2] investigated the dyeing of acetate silk by means of weak organic bases, on the basis that most of the compounds used in dyeing this fiber come in this classification, as for instance: (*A*) Various nitroamine compounds (derivatives of nitroanilines), such as Yellow 3G Paste for Acetate Silk (Badische), Celatene and S. R. A. Yellow, etc., (*B*) Numerous aminoazo derivatives, such as Yellow R Paste for Acetate Silk (Badische), and Azonine Direct Yellow 2R (Cassella); (*C*) Aminoanthraquinones such as Orange Paste, Rose R Paste, Red-Violet Paste, and Blue Paste for Acetate Silk (Badische).

Along with Meyer,[9] they support the solution theory of dyeing acetate silk on the basis of its fixation of *o*-nitroaniline, a typical weak organic base. The amount of this base fixed when equilibrium is reached, shows that the distribution coefficient between water and acetate silk is a constant for all concentrations. The color of the treated fiber is uniform throughout its cross-section which shows that it is not an adsorption process. They also point out the interesting fact that nitroaniline cannot be displaced from acetate silk by tetralin, in which it is very soluble; and that acetate silk remains colorless in solutions of *o*-nitroaniline in tetralin. Dyeing or stripping only occurs in the presence of water, the function of which is not understood. Is it not possible that the hydrolysis of nitroaniline in water, with the resulting presence of

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[d] See Chapter X.

certain active groups, may explain that function of the water? They state that the solution theory is further substantiated by the fact that all substances which are removed from water by ethyl acetate, are also able to penetrate acetate silk, whether they dye it or not. This applies to the sulfonated dyes, such as Azoflavine and the Cellit Fast dyes.

Kartaschoff[10] points out the fact that as the bases and basic dyes are electropositive, their affinity for acetate silk suggests that it is electronegative; and then he proceeds to confirm this by electrolyzing cellulose acetate in a fine state of division and in the form of a skein. The acetate silk dissolves slowly at the negative electrode and is reprecipitated unaltered at the positive pole. The phenomenon, therefore, is one of electrophoresis rather than electrolysis. However, as the dyeing is not accelerated by the use of an electric current, he believes that the electric charge does not play an important part in dyeing this fiber.

He also studied microscopically the progress of the dyeing of acetate silk, using aminoanthraquinone derivatives (Celatene dyes), and believes the process to be a simple solution of the dyestuff in the fiber, important parts being played by temperature and the presence of water. Crystals of the dye collect on the surface of the fiber first, and then dissolve gradually into it. On placing dry acetate silk fibers and solid dry dyestuffs in contact with each other for several days at 60° C. (140° F.), a permanent dyeing resulted which proves to him that the dyeing of acetate silk is a simple solution effect in which water may play a useful but not an indispensable part.

In a later paper, Kartaschoff[11] studied the acetate silk dyeing theories by colorimetric measurements of the initial and final concentrations of various purified direct cotton dyes in dye baths containing Celanese. He found that in many cases, as for instance with the phthaleins, the difference between the initial and final concentrations of the bath does not give a correct value for the amount of dye taken up by the fiber, since there is a precipitation of dye on the fiber surface, which makes difficult any sharp distinction between colloid suspensions and macrocrystalline suspensions. His results are opposed to the theory of Clavel, but

support the theory that the dyeing of acetate silk is a purely physical phenomenon due both to solution of the dyestuff in the fiber and to absorption on the surface by means of groups such as the hydroxyl and amino groups.

Contrary to Clavel's theory, he found that if the free color acid of a dyestuff is less soluble in water than its sodium salt, as for example in the case of Eosine I, Toluylene Orange, Acid Ponceau, etc., the free acid and its ethyl ester have greater dyeing powers for acetate silk than the sodium salt. Thus much deeper shades, though not altogether fast to washing, may be obtained by dyeing in a bath containing the free color acid and then passing the goods through a sodium bicarbonate bath, than by dyeing in the ordinary way. With water soluble dyes it is a general rule that the more soluble the dye is in the water, and the smaller its partition coefficient between water and ethyl acetate, the less its affinity for acetate silk (an acetate of a higher alcohol). It is an approximate rule, that whether the dye is soluble in water or not, if in comparison with its molecular weight the dyestuff is easily soluble in ethyl acetate, it will dye acetate silk effectively.

The size of the dye particle is not important, as is shown by dry dyeing, and affects only the rate of diffusion into the interior of the fiber. In the case of insoluble dyes it is shown, again contrary to Clavel's view, that a molecular dispersion will not dye the acetate silk; but the finer the suspension, the more rapid is the solubilization of the dye. With colors developed on the acetate silk fiber, such as the black obtained on treating the fiber with dianisidine, diazotizing, and coupling with *B*-hydroxynapththoic acid, it is probable that the molal solubility of the dyestuff in the fiber is less than that of the first component, so that the fiber becomes supersaturated with the dyestuff, which crystallizes out in the interior of the fiber. Owing to the insolubility of the azo color in water, it is not removed by washing. This crystallization of the dyestuff in the fiber undoubtedly accounts for the blinding or loss of luster which occasionally occurs in acetate silk during the development of such colors, in which case the color crystals are sometimes visible under the microscope.[17]

Clavel[e] studied the effect of various groups or radicals in the dyestuff molecule upon its affinity for acetate silk, and theorized that the affinity of dyestuffs for acetate silk is due to the presence of certain active groups, which, in the absence of sulfonic acid groups or if preponderating over, say, one sulfonic group present, are capable of dyeing acetate silk. He attempted to classify the dyes and radicles on this basis in the order of their numerical presidence regarding their basic or acid influence on the dye molecule; but so many factors, such as the orientation of the radicle in the molecule, the state of aggregation, etc., enter into the matter, that it is rather difficult to make a general rule covering the affinity of dyes for acetate silk.

He states that dyes of any class containing hydroxyl, amino, imino, imido, nitro, nitroso, isonitroso, acidylamino, or azo groups, and either no sulfonic acid groups, or not more than one sulfonic group together with two or more of the above groups, are suitable for dyeing acetate silk. Recent articles in the *Revue Generale des Matieres Colorantes* have extended and modified Clavel's original theory. Frank also studied this problem and found that the position (orientation) of the sulfonic group in the molecule is a very important factor.

### *The Dye in the Fiber*

Haller and Ruperti[12] report some interesting work upon the orientation of coloring matters within acetate silk and other fibers. When acetate silk is dyed at low temperatures with Para-Red, it has a yellowish shade, the dye being uniformly distributed within each fiber. After immersion in hot or boiling water, the shade becomes redder and the dye agglomerates into larger particles. Similar results are obtained, although with greater difficulty (steaming under pressure is necessary), when Para-Red is obtained from naphthol AS instead of *B*-naphthol, or when aminoazobenzene is used instead of *p*-nitroaniline.

Similar changes are observed in nitro silk dyed with the same dyes and also with Indigo, Thioindigo Red, and Indanthrene Blue.

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[e] See British Patents No. 182,830, No. 182,844, No. 226,948, and German Patent No. 355,533.

Nitro silk dyed cold with Naphthylamine Claret ($a$-naphthylamine coupled on the fiber with $B$-naphthol) contains the dye evenly distributed. When heated in water under one atmospheric pressure the dye agglomerates slightly without change of shade, but when heated for a prolonged period in boiling water or subjected to a short steaming under six atmospheres pressure, agglomeration becomes complete, the dye migrates towards the surface of each fiber and is deposited there as well-defined crystals which may be removed by washing and pressing, the fibers being thereby decolorized. Thioindigo Red dyed on nitro silk behaves similarly. Chrome Yellow, from lead acetate and a dichromate, dyed on nitro silk, is at first evenly distributed, but after steaming under four atmospheres pressure, agglomerates, and becomes orange, even in the absence of alkali, although no migration of the pigment occurs.

Similar changes are observed by steaming dyed cotton, except that the agglomerated dyes migrate to the boundaries of the lumen in each fiber as well as to the cuticle, the migration, change of shade, and condensation or crystallization of the particles of dye being favored by prolongation of the steaming or rise of temperature. Vat dyes, Indigo and Thioindigo Red easily, and Indanthrene Red 5GK, Indanthrene Brilliant Violet RK, and Indanthrene Blue RS with greater and increasing difficulty, crystallize and migrate within cotton fibers to the lumen and cuticle when steamed, accompanied by a change in shade. Uncertain results are obtained by steaming cotton dyed with direct dyes.

Alizarin Red dyed on cotton mordanted with aluminum acetate is evenly distributed within each fiber, but when steamed for an hour under a half atmosphere pressure the pigment agglomerates and migrates to the lumen and cuticle. That deposited near the cuticle is removed by washing with water, the fiber being left colorless. Under similar conditions the presence of Turkey-red oil considerably retards the agglomeration and migration, and the dye which migrates to the cuticle cannot be removed by washing. The decrease in fastness to rubbing produced by steaming cotton dyed with indigo is due to migration of the dye to the cuticle of each fiber.

Haller[13] reports work of a similar nature upon the color changes

of the blue and violet benzidine dyes on cotton, wool, and acetate silk, especially on touching the dyed cotton with a hot iron. His experiments are stated to confirm the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the cotton fiber blue, the smaller corinth-red. Solutions of a low degree of dispersion are particularly sensitive to temperature changes or to variations in the medium employed. Thus, in hot dye baths, wool and cotton are dyed red by aqueous solutions; but on cooling, the color on the bottom becomes blue-violet. Alcoholic solutions hardly affect wool but dye cotton a permanent corinth-red.

The effect of touching the dyed cotton with heated metal is to increase the degree of dispersion of the dye in the fabric, with a change of color from blue to red. The addition of hydrazine hydrate to aqueous Diamine Blue 3R solution causes a similar change, and the solution will then dye cotton corinth-red. The absorption of the dyes by fibrous alumina and barium sulfate indicates a fixed relationship between the degree of dispersion of the dyestuff and that of the absorbent. The surface of the absorbent plays a decisive part also when fibers are used, for swelling causes inner micellar surfaces to come into play, the difference in the sizes of these accounting for the different behavior of different absorbents.

Wool and acetate silk, after swelling, have larger inner surfaces than cotton. Thus an alcoholic solution of Diamine Blue 3R causes swelling of acetate silk and dyes it corinth-red. After saponification with sodium hydroxide, washing the fiber, and acidifying, the color changes to blue, showing that during saponification the inner structural conditions are changed. The reddening of blue-dyed cotton is also produced by desiccation over sulfuric acid, but to a less extent than by heating. The observed color changes on heating, and drying may thus be connected with dehydration and simultaneous increase in the degree of dispersion of the dyestuff within the fiber.

*Basic Dyes and Bases on Acetate Silk*

Among the older dyes, more products belonging to the basic group are applicable to acetate silk than those of any other one

group. The first acetate silks, consisting of primary cellulose acetate, were of such a nature that it was almost or quite impossible to dye them level and deep shades with even these dyes. Apparently the basic dyes were only taken up substantively after drastic treatment to alter or swell the fiber. Of our present acetate silks, Lustron, which is a comparatively highly acetylated cellulose, has a greater affinity for the strongly basic dyes than any other known textile fiber. Even when applied without a mordant on Lustron, some of these dyes show a greater fiber affinity and fastness than upon any other known fiber. As might be expected, the affinity of Celanese, which is not as highly acetylated as Lustron, for the strongly basic dyes is considerably less than that of Lustron. This difference in affinity for certain basic dyestuffs is sufficient under certain conditions to give medium shades on Lustron, while the Celanese remains white in the same dye bath.

The free color bases of many basic dyes may also be applied to acetate silk from colloidal suspensions, as in the dispersol method of dyeing. When applied in this manner, they frequently have a greater affinity for the acetate silk fiber than when applied as the aqueous solution of the commercial basic dyestuff. In fact many substances in colloidal solution have a high affinity for acetate silk, and this has formed the basis of the application of many of the new dyes specially developed for application to acetate silk by the dispersol process. In some cases products which have no affinity for the acetate silk fiber when they are in true solution, have a high affinity for it when they are in colloidal solution. From our study of the theory of acetate silk dyeing, this might be expected for two reasons: first, on account of the decreased solubility of the free color base in water; and, secondly, due to the lack of any retarding effect of the acid or acidic radicle used for solubilizing the ordinary basic dye. Also it leaves the color base free to combine with any acidic radicles of the acetate silk. For this reason we may expect these free color bases to have a better penetration and less "skin" effect, as they are not held on the surface by the acidic radicle of the dyestuff molecule.[1]

[1] See British Patent No. 255,962.

### *Mordanting*

Acetate silk has no affinity for the usual soluble salts of the metals used in mordanting the other textile fibers, such as chromium, aluminum or iron; nor will it take up their hydroxides to any extent, either as precipitates or as colloidal solutions. However, as discussed under the mordants,[g] it has recently been found that it does have an affinity for certain special salts of the mordanting metals, such as the thiocyanates, but these particular salts had not previously been used in mordanting, and the process is probably not yet highly successful on a commercial scale. It has no affinity for the tannins or other usual cotton mordanting agents. In the application of some basic dyes to acetate silk, certain metallic salts, such as zinc nitrate, tin, barium, and magnesium chlorides are used, as mentioned under "Assistants,"[h] but these are not true mordants. Certain colors, such as the Gallocyanines,[h] may be after treated on the fiber with metallic salts, such as chromium, to give colors of increased fastness.

### *Direct Cotton Dyes*

Acetate silk has no affinity for most of the direct cotton dyes; however, there are a few exceptions, which will be discussed with the other dyes of this class. In fact cellulose acetate resists about 60 per cent of the direct cotton dyes to such an extent that patents were at one time granted on a method of resisting cotton by means of acetylating the outer layer of the cellulose fibers. A product known as "Bayko" yarn also appears in the literature. This yarn was prepared by coating a cotton thread with a layer of cellulose acetate. Bayko yarn was used as a resist-thread effect, and even today the widest use of acetate silk is in resist-thread effects, either white or in contrasting colors, in cotton goods. In many cases where the acetate silk is stained by direct cotton or acid dyes, this staining is due to the presence of basic impurities or shading dyes.

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[g] See Chapter XII.
[h] See Chapter X.

### *Acid and Mordant Dyes*

While acetate silk has no affinity for the acid dyes as a class, largely due to the influence of the sulfonic acid group, there are a few exceptions where the other groups present have sufficient influence to overcome the effect of the sulfonic group. It also has an affinity for many dyes and other compounds containing amino, alkylamino, azo, hydroxyl, nitro and/or ketonic groups, and absorbs certain hydroxyazo dyes which contain no sulfonic groups, such as Alizarin Yellow R (*p*-nitrobenzeneazosalicylic acid) and Metachrome Brown B (2-hydroxy-3, 5-nitrobenzeneazo-*m*-phenylenediamine). Recently some special acetate silk dyes have been developed which are solubilized by means of carboxylic, arsenic, or other acid groups (other than sulfonic groups), and these belong to the acid classification. Some mordant dyes are also applicable to acetate silk and many of the slightly soluble products applied by the dispersol process might come under the acid and mordant dye classification if they were not applied by the dispersol method. As the acid and mordant dyes are applied to acetate silk by methods similar to those used for the direct dyes on cotton, they offer a rapidly growing and very interesting group for acetate silk.

By means of the saponification process of dyeing, which is no longer used except in printing, etc., it is possible to apply the direct cotton and, in fact, almost every other class of dyes used upon cotton or the older rayons to acetate silk. Possibly none of the sulfur dyes have a direct affinity for normal acetate silk, but they may be applied to the saponified fiber. Some of the vat dyes have an affinity for acetate silk, especially when applied by the dispersol method, but practically all of the vat dyes are applicable to the saponified fiber. The aminoanthraquinone dyes have a special and unexpected affinity for acetate silk, especially from a colloidal solution.[1]

### *Developed Colors*

Acetate silk has an affinity for many of the components commonly used for the production of developed or azoic colors on the cotton fiber, and these may be used for the same purpose on ace-

[1] See the Duranol and Celatene dyes.

tate silk. It has a very decided affinity for many amino compounds, particularly the primary amino bases, such as *p*-nitroaniline, aminoazobenzene, benzidine, dichlorobenzene, *o*-anisidine, *p*-aminodiphenylamine, etc. These may be applied as aqueous solutions of their hydrochlorides, as Ionamines, as an aqueous suspension prepared by neutralizing the hydrochloride in the aqueous dye bath, or by the dispersol process. They are then diazotized and developed on the fiber to give a variety of very fast colors, ranging from pale tints to black. This fact led to the development of many special products for use especially upon acetate silk, and these will be considered in detail under the developed dyes and the Ionamines. While the developed colors are not used on acetate silk at present to so large an extent as formerly, they are still used to some extent, particularly for heavy shades of the highest fastness properties, especially black. In fact, products which may be diazotized and developed are found in almost all classes of dyes used upon acetate silk.

The application of the special acetate silk dyes, the Ionamines, and dispersol type of dyes, as well as the theories evolved during the development of these products, will be discussed in connection with these dyestuffs. While the Ionamines and the dispersol type of dyes are especially well-known among the dyes for acetate silk, the advantages of some of the other special acetate silk dyes, such as the Setacyl Direct dyes, should not be overlooked.

Since the advent of the many new special acetate silk dyes, the older dyes are not now so generally used on this material, or even on the acetate silk in unions, in which acetate silk takes only a minor part. However, they are always used upon the other fibers accompanying the acetate silk in these unions and on all materials containing acetate silk effects. Therefore, while the new dyes are now used almost but not quite exclusively upon acetate silk in every form, a complete knowledge of the dyeing properties of the older dyes upon acetate silk is essential in handling unions or materials containing it. Also in dyeing colored acetate silk effects in various materials, where the acetate silk effect plays only a minor part, the older dyes are still frequently used.

The foregoing fully shows that the dyeing properties of acetate

silk are peculiar to this one fiber and that we may expect satisfactory results only from products and methods of application developed particularly for this one fiber. With the recent advances in dyes for, and methods of application to, acetate silk, it is just as easy today to obtain fast, brilliant, and pleasing shades on this fiber as on any other, provided only we use the same care in selecting the dyestuffs and in applying them that we use in dyeing the other fibers. Celanese and Lustron differ in many minor points in their dyeing properties, and probably the other English and European acetate silk fibers may each have its own individual characteristics and variations; but, as acetate silks and distinct from all other textile fibers, they are all dyed in the same general way and by the same products. For instance, the dyeing properties of Rhodiaseta are similar to those of Celanese and Lustron, in that it resists the direct cotton and sulfonated dyes, but takes the Ionamines, all of the dispersol type dyes, the Cellutyl, Cellit, Setacyl, Setacyl Brilliant, Setacyl Direct, and other special dyes for acetate silk. While Rhodiaseta is not so well known in America and to the author as are Lustron and Celanese, it is just as suitable for use as white or contrasting color effects in combination with cotton, wool, and other fibers, as the other brands of acetate silk, and it is widely used for this purpose in France and neighboring countries.

### *Phototropism*

Before leaving the theoretical discussion of acetate silk dyeing, it may be well to mention a difficulty encountered in the search for dyestuffs particularly suitable for use on acetate silk. When applied to acetate silk, many colors appear to be subject to "phototropism," a rather newly discovered property of some dyestuffs which is found almost only on acetate silk and which is not usually found in the same color on other fibers. Phototropism is the property of a color on the fiber to change in color or shade under certain lighting conditions. For instance, if the dyed acetate silk is shielded from the light for a few minutes, on removing the shield, the color is lighter beneath where the shield covered, but darkens in a short time until it matches the surrounding color.

This difficulty was encountered in the development of both the Ionamines and the dispersol type of dyes. While it is rare on other fibers, it is not entirely unknown, as for instance in the case of Fast Light Yellow on wool.

Green and Saunders[3] report that nearly all of the yellow amino-azo bases show this property on acetate silk, and though varied by substitution in the benzene nucleus, no definite relationship between the position of the substituents and the occurrence of phototropism can be traced. Apparently the greener the shade of the yellow, the more pronounced is its phototropism. The difficulty usually disappears when orange shades are reached.

The cause of phototropism in certain azoic dyes on acetate silk has never really been satisfactorily explained, but Greenhalgh[14] compares it with the desmotropism of *p*-nitrosophenol. In the case of *p*-nitrosophenol, under certain conditions the compound is white and under others it is yellow. Analysis of the yellow product shows that it is not *p*-nitrosophenol but is quinone oxamine. This change in both color and constitution is due to the transposition of a hydrogen atom in the molecule from one group to another. Greenhalgh suggests that there may be a similarity between the phototropy of certain azo dyes on acetate group and the desmotropy of *p*-nitrosophenol. It is well known that acetate silk has a high affinity for amino groups, and, while nitrogen is usually considered rather inactive, the azo coupling undoubtedly has considerable activity. In the case of certain azo dyes on acetate silk, the position or connections of this azo group may possibly be so shifted or altered, by the presence or absence of light, as to cause phototropism.

Phototropism is shown not only by the azo dyes on acetate silk, but also by some other nitrogen-containing groups, such as amino and nitro groups, and in certain cases under some conditions, it appears to be impossible to completely diazotize some amino compounds on acetate silk, which probably may be due to the high affinity of this group for the acetate silk fiber. This certainly looks as though the chemical affinity of the acidic acetate silk fiber for the basic amino group of these dyes plays some part in dyeing this fiber.

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# CHAPTER IX

## THE METHODS USED IN DESIZING, SCOURING, BLEACHING AND TINTING ACETATE SILK. DEGUMMING TRUE SILK IN THE PRESENCE OF ACETATE SILK

Just as in dyeing all other fibers, a thorough wetting-out and cleansing of the acetate silk is absolutely necessary in order to obtain the best results in either bleaching or dyeing. Where the yarn has been sized, a thorough removal of all sizing materials is of course the first step in the process. A number of desizing and scouring methods and formulas have been suggested and used on acetate silk with just as varied results. Where the material to be scoured contains another fiber in combination with the acetate silk, this serves to complicate the process somewhat. From the foregoing study of the properties of the acetate silks it is very evident that the scouring process for Lustron may be somewhat more severe than that for Celanese or Rhodiaseta. Yet even on Lustron we cannot employ either strong or caustic alkalies, and undoubtedly much better results, as regards the textile properties of the fiber, are obtained by using mild detergents at medium temperatures.

The manufacturers[2] of Celanese strongly caution against the use of either high temperatures or free alkali in any process on Celanese. However, Grimshaw[1] states that Celanese will not lose its luster on treating it for 30 minutes with as much as four ounces of soda ash per gallon of water, at temperatures below 80° C. (176° F.). The Lustron Company state that their product will withstand the usual natural silk boil-off and that as much as 5 per cent of sodium carbonate may be used in fulling at temperatures below 60° C. (140° F.). A very important thing to remember in scouring, bleaching, dyeing, or in any other wet process on acetate silk, is that it should be handled like true silk, rather than like cotton. This is particularly important in skein scouring, dyeing, or other

wet processing of fine denier yarn, otherwise serious trouble may be experienced in winding.

In scouring Rhodiaseta, as well as in dyeing it, the same care, as regards the temperature and alkalinity of the bath must be exercised as in handling Celanese. The luster and brilliancy of Rhodiaseta may be impaired considerably by scouring above 80° C. (176° F.), or in the presence of alkalies, such as sodium carbonate, in high concentrations, unless special precautions are taken as described later.

It is of course obvious that in no operation on any variety of acetate silk or on any material containing it, can we use any process similar to kier boiling. This of course means that on cotton-acetate silk unions, or even cotton goods containing acetate silk effects, the cotton must be scoured by a less drastic method than kier boiling. Grimshaw[1] found that such sizing materials as modified corn starch, Celanese size, gelatin, potato starch, or a combination of gelatin, starch, and glucose, were much easier to remove from the Celanese of Celanese-cotton unions, than from the cotton.

The usual Celanese-cotton scour, as given in Method No. 6 below, but for two hours, removes the sizing materials completely from Celanese; but the iodine test shows starch still present on the cotton in sufficient quantities to prevent a good white on bleaching by the usual methods. Even a soap-and-soda-ash scour, such as used on viscose-cotton unions, but at 80° C. (176° F.), failed to completely remove the size from the cotton. For this reason he recommends the use of an enzyme steep as in Methods No. 1 or No. 3, before scouring. Method No. 2 is very similar. The goods should then be scoured for one hour by his modification of Method No. 6, as given in Method No. 7. When desized and scoured by these methods, a good white is obtained upon both the cotton and Celanese by bleaching as in Method No. 15, either with or without acetic acid. The antichlor treatment, as given in Method No. 18, may be used to advantage. Grimshaw[1] also states that the sizing materials may be removed by Method No. 4.

Where gelatin is a constituent of the acetate silk sizing mixture, care must be taken to see that all of this sizing material is removed

before attempting to dye the material.[6] Gelatin is a protein and as such has dyeing properties somewhat similar to those of wool. The dyeing properties of acetate silk approach those of wool more nearly than those of any other fiber in many respects. For this reason many of the acetate silk dyestuffs dye wool and gelatin, with the result that if the gelatin sizing material is not thoroughly removed before the rayon enters the dye bath, quite unexpected results, as to color, are frequently obtained. One of the best methods of removing gelatin is to first soak the sized rayon in cold water for some time and then warm up the bath gradually, so as to bring the swollen gelatin into solution.

No matter what process is used in desizing, scouring, or bleaching acetate silk, care must be taken to avoid the hydrolysis or saponification of the ester, which results in a complete change of dyeing properties and affinities, with the consequent uneven shades. A discussion of the properties of this saponified or partially saponified acetate silk and the methods of detecting it are given in Chapter XIX, on the Saponification Method of Dyeing Acetate Silk.

### *Desizing Acetate Silk*

*Method No. 1: Removal of Size.* Steep in an aqueous bath containing 50 grams per liter of diastofor at 60° C. (140° F.) for about 30 minutes. (Possibly better than Method No. 3.)

*Method No. 2: Removal of Size.* Work for 30 to 45 minutes in a bath containing 4 to 8 pounds of diastofor per 100 gallons, at 60 to 71° C. (140 to 160° F.). The skeins may then be taken out and piled overnight. If a standing bath is used, replenish the bath with one-third to one-half of the original charge of diastofor. In case the bath is alkaline, correct this with acetic acid.

*Method No. 3: Removal of Size.* Steep in an aqueous bath containing 35 grams of rapidase per liter at 80° C. (175° F.) for 15 minutes.

*Method No. 4: Removal of Size.* Pad the goods in a hot aqueous solution of soluble oil. Roll them up and allow them to stand overnight. Then scour for at least an hour as in Method No. 6.

*Scouring Methods*

*Method No. 5: Scouring Celanese Alone.*[2] Scour in a bath containing 1.25 to 1.5 grams of olive oil soap and either 1 cubic centimeter of 20 per cent ammonia or 0.25 gram of sodium carbonate per liter at 75 to 80° C. (167 to 176° F.) for one-half to one hour. Rinse well in warm water and then in cold water. The sodium carbonate should not amount to more than 2 per cent, on the weight of the Celanese.

*Method No. 6: Scouring Celanese-Cotton Unions.*[2] Scour in an open tub at not over 80° C. (176° F.) for forty-five minutes to two hours in a bath containing 2.5 grams olive oil soap, 2.5 grams of 50 per cent Turkey-red oil, and 1 cubic centimeter of 20 per cent ammonia per liter. Then rinse well, as in Method No. 5, and it is ready for bleaching by Method No. 15.

*Method No. 7: Grimshaw's*[1] *Modification of Method No. 6.* Scour for an hour at about 80° C. (176° F.) in a bath containing 2.5 grams per liter of olive oil soap and an equal amount of emulsified mineral oil, such as is used in raw silk scouring.

*Method No. 8: Scouring Lustron-Cotton Unions.*[3] The manufacturers of Lustron recommend that it should be scoured with 10 per cent of neutral olive oil soap and 1 per cent of soda ash, on the weight of the goods, for about one-half hour at a maximum temperature of 80° C. (176° F.).

*Method No. 9: Scouring Lustron-Cotton-True Silk Unions.*[3] Unions containing Lustron and real silk in the gum may be boiled off in one or two changes of a three-quarters to one per cent neutral olive oil soap solution for about one hour at 93 to 96° C. (200 to 205° F.).

At the present time there are a wide variety of scouring agents offered upon the market, many of which are excellent for certain special purposes on various textile materials. Many of these compounds are liquid combinations of soaps and solvents, and some contain free alkalies. Considering the nature of acetate silk, it is almost impossible to predict just what the action of some of these solvent scouring agents will be upon this fiber and therefore they should be used with extreme caution until complete tests, including dyeing and finishing, have been made upon the scoured fiber.

*Celascour*

Celascour was developed and placed upon the market by the manufacturers of Celanese particularly for use upon Celanese and materials containing it. This compound is probably similar in composition to some of those described above, i.e., a special mixture of soap or Turkey-red oil, with or without solvents, possibly very slightly alkaline. It is used both as a pretreatment or scour before dyeing,[2] and in the S.R.A. dyebath, as an aid to leveling and penetration. In use, it is merely diluted with hot soft water and added to the soap scour or dye bath in the proportion of 0.5 to 5.0 cubic centimeters per liter of bath. These baths are used in the same manner and at the same temperatures as those without the Celascour, as in Methods No. 5 and No. 6. After the operation, the acetate silk should be rinsed free of soap with soft water.

Methods No. 10, No. 11, No. 12, No. 13, and No. 14 are given by various dye manufacturers as satisfactory for acetate silk, variety not stated. They are given here for comparison.

*Method No. 10: Scouring Acetate Silk Alone.* Scour in a 25 to 1 bath with 5 to 12 per cent of olive oil soap and 0.5 to 1 per cent of soda ash, on the weight of the material, at 60° C. (140° F.) for 30 minutes. Rinse hot and cold, if necessary, in water slightly acidified with acetic acid.

*Method No. 11: Scouring Acetate Silk Knitted Fabrics.* In scouring knitted fabrics which usually contain more or less oil, up to 1 gram of soda ash and 1 to 3 cubic centimeters per liter of a Turkey-red oil solvent hydrocarbon emulsion, such as are now common on the market, may be added to the above, Method No. 10. (Some of the hexalin or tetralin scouring emulsions, such as Isomerpin, are widely used and should be excellent for this purpose. Celascour is also recommended.)

*Method No. 12: Scouring Acetate Silk Alone.* Scour at 45° C. (113° F.) with a solution containing 2 per cent of hard soap and 4 per cent of ammonia, on the weight of the fabric, for 20 minutes. Rinse in two waters, sour in a bath containing 2.5 per cent of 30 per cent hydrochloric acid, on the weight of the goods, and finally rinse.

*Method No. 13: Scouring Acetate Silk-Cotton Unions.* Still another variation for unions is recommended. Scour at 75° C. (170° F.) in a bath containing 1 or 2 pounds of Monopole soap per 100 gallons of liquor. If the cotton is unbleached use a slightly higher temperature, 80 to 85° C. (175 to 185° F.), and rinse the goods as in Method No. 5.

*Method No. 14: Scouring Celanese.* Scour in a solution containing one-half pound each of soap and ammonia, to each ten gallons of liquor, at 65° C. (150° F.) and rinse as in Method No. 5.

### *Bleaching Acetate Silk*

Where pale or brilliant shades are to be dyed, it may be necessary in some cases to bleach the fabric containing acetate silk. The manufacturers of Celanese recommend that this should be done by Method No. 15.

*Method No. 15: Bleaching Celanese.*[2] Treat for one hour in a cold 0.25 Tw. sodium hypochlorite solution. This bath may be prepared as in Method No. 16 or from soda ash and chlorine, as for the regular cotton bleach. The bath may be either neutral or acidified slightly with acetic acid just before using. If the neutral bath is used, the goods may be acidified in a separate dilute acetic acid bath after leaving the bleach. The bleached Celanese should then receive an antichlor treatment, as given in Method No. 18.

*Method No. 16: Bleaching Lustron-Cotton-Viscose Unions.*[3] The Lustron Company advise the use of hypochlorite on either Lustron-cotton or Lustron-cotton-viscose unions. Prepare a stock hypochlorite solution from 10 pounds calcium hypochlorite (bleaching powder) and 6 pounds soda ash in 50 gallons of water. Allow this to settle and use the clear liquid.

Make up the bleach bath for use at 0.5 to 0.75° Tw. (1.0025 to 1.004 sp. gr.) from the above clear liquor or from soda ash and chlorine direct, as mentioned in Method No. 15. After scouring as in Method No. 8, bleach in this bath at 25 to 30° C. (77 to 86° F.) for 1 hour. Rinse lightly and sour in a cold 0.5 per cent acetic acid solution for 15 or 20 minutes. Work until neutral, then neutralize in a bath containing 0.25 per cent of sodium bicarbonate

for one hour. Hydroextract and dry without rinsing, or if the goods are to be dyed, rinse and proceed with the dyeing. A standing bleach bath may be used to advantage.

*Method No. 17: Combination Scouring and Bleaching.* A shorter combination method of scouring and bleaching in a single bath at one operation has been suggested. In this process, about 2.5 cubic centimeters of sodium hypochlorite is added to each liter of scouring liquor, so that the scouring and bleaching proceed simultaneously. In using this method, particular care must be taken to be absolutely sure that the hypochlorite solution is free of calcium salts, as in the presence of soap, these are sure to cause spots on the material during dyeing. No matter what method of hypochlorite bleaching is used, the bleach bath should not contain any calcium salts.

### *Antichlor Treatment*

In bleaching any variety of rayon, and especially acetate silk, with hypochlorite, it is particularly important that every trace of chlorine be removed from the bleached fiber, by the use of suitable antichlors and thorough rinsing.

*Method No. 18: Antichlor Treatment for Celanese.*[2] The Celanese manufacturers recommend that after the hypochlorite bleach, as in Method No. 15, the Celanese should have an antichlor treatment for 15 minutes in a cold bath containing 0.5 to 1 gram per liter of sodium bisulfite. This should be followed by a thorough rinsing.

### *Peroxide Bleaching*

Besides the above bleaching methods, the Lustron Company state that acetate silk may be bleached with peroxide and particularly recommend this method for unions containing true silk or wool. The hydrogen peroxide bleach on acetate silk, or unions containing it, is conducted in practically the same way as in bleaching wool, except that as usual in all wet processes on acetate silk, the peroxide concentration should be somewhat higher than that used for wool.

*Method No. 19: Hydrogen Peroxide Bleach on Acetate Silk.* The bath may be prepared with a concentrated solution of hydro-

gen peroxide or as follows: To prepare 100 gallons of bleach bath, add to each 97 gallons of cold water, 11 pounds of 56 per cent iron-free acetic acid. Sprinkle sodium peroxide slowly into this bath while stirring well to prevent undissolved peroxide from sinking to the bottom of the vat. When about half of the peroxide has been added, start heating the bath slowly to 38° C. (100° F.). Continue adding sodium peroxide while heating until the bath reacts neutral to litmus paper. Usually about 4 pounds of sodium peroxide are required to make up the neutral bleach bath. When the neutral point is reached, heat the bath to 49° C. (120° F.) and add 2 pounds of Monopole oil. Mix well and enter the goods as quickly as possible at 49° C., maintaining this temperature until the proper bleach is obtained. In the case of Celanese, the temperature should be held at 38° C. (100° F.). Where ammonia or sodium silicate is used in the peroxide bleach bath, only sufficient may be added to render the bath very faintly alkaline. After bleaching, rinse first in water at 38 to 49° C. (100 to 120° F.) and then in cold water.

*Method No. 20: Permanganate Bleach on Acetate Silk.* The permanganate method of bleaching may also be used on acetate silk. This bleach bath should be prepared with 1 pound of sodium or potassium permanganate per hundred gallons of hot water. The scoured acetate silk is worked cold in this bath for two or two and a half hours. As this bath becomes alkaline to litmus paper in use, acetic or sulfuric acid should be added to keep it very slightly on the acid side while the acetate silk is present. Usually about 100 to 200 cubic centimeters of concentrated sulfuric acid will be required for each pound of permanganate used.

After the permanganate bleach, the brown manganese dioxide stains may be removed from the fibers by working them for from 30 to 45 minutes in a cold bath containing 4 pounds of sodium bisulfite and up to 2 pounds of 66° Be. sulfuric acid in 100 gallons of water. If the acid is omitted, the clearing bath may be warmed somewhat to accelerate the reaction, or the amount of bisulfite may be doubled. When the skeins are white, they should be rinsed with fresh water until colorless.

Feibelman[5] states that the rayons may be bleached with aktivin,

which is the sodium salt of toluene-*p*-sulfochloroamide, without injury. Neutral solutions containing even 3 or 4 per cent of aktivin at 60 to 70° C. (140 to 158° F.) do not affect either the luster or strength of rayon, although they bleach it only to a uniform cream color. Acid solutions of this strength give a full white. For example, 3 grams of aktivin are dissolved in a liter of water and 5 cubic centimeters of acetic or 50 per cent formic acid are added. The slightly turbid solution has a stronger bleaching action than aktivin itself and the rayon is not injured, even at high temperatures. Bleaching is complete in a half-hour and the material should then be treated with a bisulfite solution, before washing. While there is no apparent reason why this method should not be satisfactory on acetate silk, nothing definite has been given regarding its use on this fiber.

It is interesting to note that Greenhalgh[4] reports instances of the "pinking" of acetate silk after bleaching when improperly washed, due to the presence of substances other than cellulose acetate, such as aniline, toluidine or xylidine, in the fiber. He states that the pink stains are the result of the oxidation of these or similar compounds, that the color is analagous to that of Magenta, and that the stain may be removed by soaping or by a further light bleach.

### *Bluing or Tinting Acetate Silk White*

In case the acetate silk is to be used undyed and it is desired to improve the natural color without an actual bleaching operation, the fiber may be blued by tinting it in a bath containing a violet or blue dye of a reddish shade. The dyes most frequently used for this purpose are the Methyl Violets and Indanthrene Violets or Blues, although certain other dyes could be used for the purpose. In case the Indanthrene dyes are used, the prepared thick dye paste is simply diluted with water and added directly to the "bluing" bath without reduction.

### *Degumming True Silk in Acetate Silk Combinations*

Before dyeing combinations of acetate silk with true silk it is frequently necessary to boil-off the true silk as well as desize the acetate silk. In the case of Lustron, this boil-off may take place

in the usual boiling neutral soap degumming bath without injury to the acetate silk. In the case of Celanese there are several methods of degumming without injury to the acetate silk, some of which are patented processes. It is obvious that in the case of Celanese or Rhodiaseta, temperatures of over 85° C. (185° F.) should not be used in degumming without special precautions, as mentioned in British Patents No. 206,113 and No. 246,879.[a] Each of the following methods has its advantages for certain classes of work.

*Method No. 21: Degumming True Silk in the Presence of Celanese.*[2] Impregnate the material with a strong aqueous solution of Turkey-red oil (50 per cent of fatty acids) containing 1 to 3 per cent of sodium carbonate or its equivalent of sodium silicate, phosphate, or borate, at 75° C. (167° F.). Squeeze until the material contains only about its own weight of liquor and allow it to lay for 6 to 12 hours. Scour off twice at 75° C. in a solution containing 0.25 per cent of sodium carbonate and then rinse well with hot soft water

*Method No. 22: Degumming True Silk in the Presence of Celanese.*[2] Prepare an 80° C. (176° F.) steeping bath containing 1 per cent of olive oil soap and enter the union, allowing it to remain about 12 hours. Then add about another 1 per cent of the soap, on the weight of the bath, and about 0.25 gram per liter of sodium perborate, raising the temperature again to 80° C. Allow this to stand for several hours more, heating to 80° C. and adding the same amount of perborate again, if necessary, and work the goods carefully until the gum is removed. Then rinse free of soap.

*Method No. 23: Degumming True Silk in the Presence of Celanese.*[2] Prepare a 30 to 1 degumming bath containing 1 per cent of olive oil soap, on the weight of the bath. Add 1.5 per cent of sodium phenolate, on the weight of the goods, and treat the material at 80 to 85° C. (176 to 185° F.) for 2 hours. Rinse well with hot soft water.

According to British Patent No. 206,113, July 11, and German Patent No. 395,829, June 17, 1923, to the Société Chimique des Usines du Rhone and the Société pour la Fabrication de la Soie

[a] See Chapter XXV.

"Rhodiaseta," it is not always necessary to degum true silk at temperatures below 85° C. when acetate silk is present. While both Rhodiaseta and Celanese are usually delustered on treatment with aqueous solutions above this temperature, these patents by the manufacturers of Rhodiaseta state that fabrics made from acetate silk either alone or in combination with raw true silk, may be degummed or/and desized without injury to the acetate silk by adding a neutral potassium salt, such as the chloride, sulfate, or dipotassium phosphate, etc., to the soap bath. It is claimed that the potassium salts, in the presence of salts of other metals, protect the acetate silk without retarding the foaming of the soap solution, and that the degumming and/or desizing may take place at the boil without detriment to the acetate silk in any way. A suitable degumming bath for use on an acetate silk—true silk unions may contain 0.5 to 2 per cent of neutral soap and 10 per cent of the neutral potassium salt, on the weight of the bath. The treatment is carried out at 90 to 100° C. (194 to 212° F.) until the gum of the true silk and the size of the acetate silk are removed, which usually requires 30 to 60 minutes. If the true silk contains much gum, a second treatment with a more dilute soap bath may be given. Very possibly some modification of this process could also be used in dyeing Rhodiaseta and Celanese at high temperatures. See British Patent No. 246,879 which may also be used in degumming.

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# CHAPTER X

## THE BASIC DYES ON ACETATE SILK

*The Methods of Applying the Basic and Gallocyanine Dyes to Acetate Silk. The Use of "Assistants" and Patents Covering Same. The Ammonium Thiocyanate Method*

EARLY in the development of acetate silk it was well known that it absorbed a few dyes substantively, but these were mainly basics. Some of these basic dyes possess a fastness to light and washing on certain acetate silk which is rather unexpected and entirely out of relation to their fastness on other fibers, even without a mordant. However, the affinity, and therefore the fastness properties, of the various basic dyes, varies with the different brands of acetate silk. For instance, Lustron has the highest affinity for the basic dyes of any known commercial textile fiber, while Celanese does not have such a high affinity for them. The difference is so great that with certain dyes under suitable conditions, the Celanese, as well as all other fibers, may be left practically unstained in a basic dye bath in the presence of Lustron. For example, if Lustron and Celanese are dyed together in the same bath with a basic dye, such as Rhodamine or Malachite Green, the Lustron will take on a very full shade while the Celanese will be dyed only a comparatively light shade.

Very possibly the affinity of the acetate silks for the basic dyes is largely due to their sulfate and acetate groups and the difference in the affinity of the two varieties mentioned above may largely be due to the differences in their composition, although the finishing process may play some part in the difference. The fastness of the basic colors on acetate silk appears to follow closely the affinity of the basic dyestuff for the acetate silk and for this reason we may rightly expect the basic dyes on Lustron to have better fastness than on Celanese. Even the light fastness of many of the unmordanted basic dyes is unexpectedly good on Lustron.[7]

Dort,[1] the American authority on dyeing Celanese, points out that while some basic dyes really dye Celanese, others only stain it, and that only in a limited sense can Celanese be dyed with basic dyes. From the discussion in Chapter VIII on the application of basic dyes to acetate silk, this is to be expected, as is also the fact mentioned by Dort, that the fastness properties of the basic dyes on Celanese is entirely different from these properties on other fibers and frequently unsatisfactory. He cautions that the basic dyes should not be used on Celanese except under unusual circumstances and with the most careful control and supervision.

On account of the high affinity of the basic dyes for Lustron it is possible to cross-dye basic colors on Lustron-cotton, silk, or wool unions, which will not withstand cross-dyeing on Celanese. With many basic dyes it is impossible to obtain heavy or even medium shades on Celanese without the assistance of special dyeing methods or chemicals, such as those described under "Assistants."

The extreme difficulty in evenly dyeing the earliest acetate silk was undoubtedly due to the particular chemical character of the product in use at that time. Cellulose triacetate is extremely difficult to wet-out, due to its high interfacial surface tension against all neutral or acid aqueous solutions, while the strongly alkaline solutions react chemically upon the acetate. Even the present products are more difficult to wet-out than the ordinary textile fibers in the dye bath, and for this reason it is important that the acetate silk should be thoroughly wet-out in a separate scouring bath before it enters the dye bath. The still wet acetate silk should be entered into the basic or other dye bath before there is any possibility of its becoming dry in spots, or these spots will dye considerably lighter with most dyestuffs.

All the usual precautions required in applying the basic dyes should be exercised in applying them to acetate silk. Where several dyes are to be used in the same dye bath, the usual care in selecting dyes which do not precipitate each other must be taken. Where such precipitation occurs, the dyes may be applied in separate baths, instead of in one dye bath, and in some instances the fastness to water and washing may be greater than that of either

component dye alone. Sodium hydroxide, and to a less extent sodium carbonate and soap, causes precipitation of certain basic dyes. These chemicals may also act upon the acetate silk and therefore should not be present in the basic dye bath.

Where the dyestuff is difficult to dissolve, it should be made into a paste with dilute acetic acid or glycerol and a little alcohol. This paste may be diluted with warm water, dissolved in hot water, and finally added to the dye bath by filtering through a fine piece of cloth. Basic dyes which are dulled by metals should not be applied in iron, copper, or other metals which react with them. Low temperatures in the application of the basic dyes is desirable from the standpoint of the dyestuff as well as the acetate silk.

Neutral sulfonated or monopole oil is frequently useful in the basic dye bath as an aid in leveling and penetration. Glucose, acetin, and diastofor are also claimed to be of value in leveling the basic dyes on acetate silk. Both glucose and acetin may be used in the basic dye bath with zinc salts, which will be mentioned later. Silk boil-off liquor is absolutely useless in dyeing acetate silk. Possibly some of the new wetting-out agents, such as Celascour, Isomerpin, Nekol A, etc., may be useful either in the dye bath as an aid to penetration and leveling, or in previously wetting-out the acetate silk. In selecting these wetting-out assistants, care must be taken to avoid those containing solvents which may act upon the acetate.

The presence of organic acids, such as acetic, formic, tartaric, and lactic acid, and certain neutral salts, such as sodium or ammonium sulfates, chlorides or acetates, in the basic dye bath tends to retard the absorption of dye by the acetate silk. Sodium chloride and acetic acid are usually the most satisfactory for this purpose. This fact appears to support the statement of Greenhalgh[2] that the acetate silk is dyed only by the basic radicle of the basic dyes and not by the soluble compound of the basic dyestuff as a whole, the acid portion of the basic dyestuff molecule remaining in the dye liquor. The mineral acids should never be substituted for the organic acids in dyeing acetate silk.

The usual bottom mordanting with tannin, Katanol, etc., widely

used for basic dyes on cotton, is useless on acetate silk but some special compounds are useful in obtaining deeper and faster shades, and these will be mentioned later. Owing to the low specific gravity of acetate silk it does not sink much in water so that particular care must be taken to keep it submerged in the dye bath.

The di- and triphenylmethane dyes have a good affinity for Lustron, the former being the most useful, as for instance Malachite Green, Magenta, and Chrome Violet. Increased methylation of the di- or triphenylmethane dye appears to decrease its fastness on acetate silk, possibly due to the increase in molecular weight. The thiazine dyes, such as Methylene Blue, are not usually so satisfactory; but the oxazine dyes, which contain an atom of oxygen in place of the sulfur atom present in the thiazine dyes, are useful. Suitable oxamine dyes are Nile Blue, Capri Blue and New Methylene Blue.

As is the case with all other classes of dyes on every fiber, the fastness of the individual members of the basic group varies considerably, not only with the individual dye itself, but also with the variety of acetate silk to which it is applied. For this reason it is difficult to give much definite information regarding the fastness to the various factors upon the different varieties of acetate silk. Acetate silk is more transparent to the ultraviolet light rays than any other textile fiber, and this characteristic may bring out another variation from the usual routine of light fastness tests.

On account of the higher affinity of the basic dyes for Lustron, in applying these dyes to it, longer dye baths, more retarding agent, or/and lower dyeing temperatures must be used than in dyeing Celanese, in order to prevent unevenness. In many cases one per cent of the basic dye will give a deep shade on Lustron. The following is a partial list of the many basic dyes which have been suggested for use upon acetate silk. It is compiled from a wide variety of sources and of course the affinity of the different products varies considerably. The dyes starred are particularly fast to light on acetate silk although some of the others may be equally fast.

*Blue*

Thionine Blue
*Tannocyanine B
*Cresyl Blue 2RN, and 2BS, and 2RS
*Brilliant Cresyl Blue BB
Rhoduline Blue 5B, 6B conc., GO, 3GO
Tannoturquoise BB
Rhoduline Sky Blue BB and 3G
Brilliant Rhoduline Blue R
New Blue DA conc.
*Turquoise Blue G and BB (very good)
*Fast Blue RS
*Capri Blue GON
Medola Blue
Victoria Blue
Methylene Blues (not satisfactory on Celanese)
Night Blues
Nile Blues
Indoine Blue 2RD
Cotton Blue 2B
New Methylene Blue F
New Blue 13535 and R conc.
Fast Navy Blue R
Setocyanine
Setoglaucine (very good)
Indoine B and 3B
Acronal Brilliant Blue (very good)

*Green*

*Green Yellow shade 32
*Imperial Green GI
*Malachite Green (very good)
Ethyl Green
*Brilliant Green crystals C.I. No. 622 (very good)
*Victoria Green WB
*China Green crystals
Methylene Green B, DG, G, GG, and O
Solid Green crystals O

*Yellow*

*Rhoduline Yellow T and 6G
*Janus Yellow R
*Auramines
Thioflavine T, TG, and TG extra
Coriphosphine O and OX
Phosphines
Auracine G
Methylene Yellow
Flavophosphines
Acridine Yellow 2R and GR

*Orange*

Rhoduline Orange N and NO
Chrysoidines (very good)
Tannin Orange R powder
Acridine Orange (very good)

*Red*

*Magenta (very good on Lustron)
*Fuchsine
*Rhodamines B, 3B, 6G extra and S (very good)
*Rubine Crystals
*Diamond Fuchsine
*Acridine Red 3B
*Pyronine G
*Rosazeine B extra and 6G extra
Rhoduline Red G
Brilliant Rhoduline Red B
*New Magenta Crystals
Safranines
Brilliant Safranine G conc.
Induline Scarlet

*Violet*

*Methyl Violets
Methylene Violet
*Crystal Violets
Ethyl Purple 6B
Ultra Violet (a gallocyanine)
*Brilliant Heliotrope 2R conc.
*Rhoduline Heliotrope B and 3B
*Methylene Heliotrope
Brilliant Rhoduline Purple R
Tannin Heliotrope

*Brown*

Vesuvine conc.
Bismark Browns

*Grays and Blacks*

Prune Gray
Methylene Gray B New
Chrome Gray
Artificial Silk Black
Basic Black FCG and SB

Some of the Janus dyes are also applicable to acetate silk, however most of them give rather dull shades and require a comparatively high temperature in the dye bath, which in the case of Celanese or Rhodiaseta may injure the luster. They are not particularly fast on Celanese. Chrome Blue is a chrome developing dye which is sometimes used with the basic dyes on acetate silk. Only small quantities of it may be used in the same dye bath with the basic dyes. As it is affected by metals, copper should not be present. It has a very high affinity for acetate silk so that care must be used to avoid unevenness.

*Dyeing Methods for the Basic Dyes on Acetate Silk*

There are a number of methods for applying the basic dyes to acetate silk, but most of them vary only in the minor details. In order to give some idea as to the different variations offered, the following methods are given. It should be remembered that many neutral salts, as well as the organic acids, act as retards for the basic dyes on acetate silk.

The British Celanese Company formerly recommended that both the basic and gallocyanine dyes be applied to Celanese with acetic or formic acid and sodium chloride, using either soft or hard water. While the exhaustion of dyestuff is not nearly complete by this method, the brilliancy of shade obtained is often very desirable. The basic dyes are frequently used for topping other dyes on acetate silk, just as they are used on cotton and other fibers to secure brighter colors. More will be given in regards to topping later. A 25 or 30 to 1 dye bath is usually satisfactory for most basic dyes on Celanese. After dyeing the acetate silk should always be rinsed and given a light soaping at 45° C. (113° F.). The following formulas are typical:

*Method No. 24: Basic and Gallocyanine Dyes on Celanese.* Enter the material at 45° C. (113° F.) in a 25 to 30 to 1 dye bath containing about 1 cubic centimeter of acetic acid (100 per cent) per liter, about 30 per cent of sodium chloride (on the weight of the goods) and the required amount of dyestuff. Dye up to two hours at 45 to 80° C. (113 to 176° F.), or until the desired shade is obtained. After dyeing always rinse the acetate silk well and

soap it lightly at 45° C. to avoid crocking. With the above formula a saxe shade may be obtained with 0.3 per cent of Capri Blue GON and 0.006 per cent of Magenta Crystals; or a Deep Royal color with 1.5 per cent of Prune Pure.

*Method No. 25: Basic Dyes on Lustron.* The basic dyes are applied to Lustron in approximately the same manner as in the above Method No. 24, except that a 30 or 40 to 1 dye bath, with more retarding agent, such as acetic acid should be used, and the Lustron entered cold. The temperature of the dye bath may then be increased gradually to 80° C. (176° F.). Lactic and tartaric acids have also been mentioned as retards for Lustron but do not appear to have any advantage over acetic acid. Of course it is easier to obtain level medium and full shades than tints.

*Method No. 26: Basic Dyes an Acetate Silk with Acetic Acid.* Prepare the dye bath with 2 to 4 per cent of acetic acid, on the weight of the material to be dyed, and the required amount of dyestuff at 38° C. (100° F.). Enter the acetate silk at this temperature and work it for about 30 minutes. Then raise to 60 to 71° C. (140 to 160° F.) and dye at this temperature until the bath is exhausted.

*Method No. 27: Basic Dyes on Acetate Silk with Ammonium Salts.* Use at least a 20 to 1 or preferably a longer dye bath containing ammonium chloride, sulfate or acetate, and the dyestuff. Enter the acetate silk cold, raise the temperature to 60 or 70° C. (140 or 158° F.) in about a half hour and hold it there for the same length of time, when more ammonium salt, in solution, is gradually added to aid the exhaustion, until about 30 to 50 per cent of the salt is present in the dye bath. Also see Method No. 41 on the application of acid and mordant dyes with ammonium salts.

*Method No. 28: Basic Dyes on Acetate Silk with Magnesium Chloride.* Enter the acetate silk cold into the dye bath containing 1 or 2 per cent of acetic acid and 5 to 20 grams per liter of either magnesium or sodium chloride. Heat the dye bath gradually so that in about an hour a temperature of about 80 or 85° C. (176 or 185° F.) is reached. Finish in water containing acetic, formic, or tartaric acid. A "scroop" finish may be obtained by adding a little olive oil emulsion to the acid finishing bath.

### *Dyeing Acetate Silk with Various "Assistants"*

The fact that tannin and other mordanting agents, such as are used upon cotton in applying the basic dyes, are useless upon acetate silk was mentioned before. However certain other compounds, which are possibly best described as "assistants," are useful in obtaining deeper shades and increasing the fastness to water, soaping, etc. Most of these assistants are salts, usually inorganic, although some organic compounds have also been patented for this purpose, as will be seen from the patents which follow later.

The assistants are compounds which form double salts with the basic dyes. These double salts appear to be less soluble in water and more soluble in acetate silk than the basic dyestuff alone, with the result, as mentioned in Chapter VIII, that much deeper and faster shades are obtained. Pokorny[3] mentions that acetate silk which has been treated with a 6 per cent aqueous solution of resorcinol also gives deeper shades with the basic dyes than the normal fiber, and states that the action is a partial deacetylation of the fiber. While the process is rather expensive it may have some use for printed color effects.

### *Celloxan*

Celloxan is a viscous liquid produced by Bayer and Company for use in applying the basic dyes to acetate silk and contains a large proportion of zinc nitrate.[a] Its application is very simple as shown by Method No. 29 which covers this process. Celloxan does not impair the luster, handle, or strength of the acetate silk and has no saponifying action. The resulting shades are stated to have a good fastness to washing. The Katanol or tannin aftertreatments given in Methods No. 32 and No. 33 are claimed to increase the fastness of basic dyes, when applied either with or without Celloxan.

*Method No. 29: Application of Basic Dyes with Celloxan.* Dissolve the dyestuff in the usual manner and add it to the 20 to 1 dye bath at about 70° C. (158° F.). Then add the proper quantity of Celloxan as given in Table XXIII. Enter the acetate silk and dye for about three-quarters of an hour at 70° C. After dyeing, hydroextract, rinse well, brighten in a bath with 1 per cent of

[a]See British Patent No. 216,838, which possibly covers this process.

acetic acid at 40° C. (104° F.), and dry at 30 to 40° C. (86 to 104° F.). When a standing bath is used, it is usually necessary to add only about half the original quantity of dye and Celloxan to replenish the bath. In the case of the dyes marked *, it is advisable to add the Celloxan in two portions, adding one-half of the quantity at the start, and after about fifteen minutes add the remainder. The dyes marked † are particularly fast to light.

TABLE XXIII

AMOUNT OF CELLOXAN TO BE USED IN APPLYING THE VARIOUS DYES

| *Name of Dyestuff* | *Cubic Centimeters of Celloxan per Liter of Dye Bath for a 2% Dyeing* |
|---|---|
| *Yellow* | |
| Auracine G | 10. |
| †Auramine O | 20. |
| Auramine G | 20. |
| Coriphosphine O and OX | 15. |
| †Rhoduline Yellow T and 6G | 15. |
| *Orange* | |
| Chrysodine G extra and R extra | 15. |
| Rhoduline Orange N and NO | 15. |
| *Red* | |
| †Rhodamine 3B | 15. |
| *†Rhodamine 6G extra | 6. |
| Rhoduline Red B | 15. |
| * Rhoduline Red G | 5. to 7.5 |
| *†New Fuchsine | 10. to 15. |
| *†Diamond Fuchsine | 10. to 15. |
| Safranine FF extra | 10. |
| *Brown* | |
| Bismark Brown FR extra | 20. |
| *Violet* | |
| †Brilliant Rhoduline Violet R | 4. to 5. |
| *†Crystal Violet P | 10. |
| *†Methyl Violet 1B, 2B and 4B | 4. |
| *†Methyl Violet 5B and 6B | 5. |
| *†Methyl Violet 1R and 4R | 4. |
| *†Rhoduline Heliotrope B and 3R | 10. |
| *Blue* | |
| Methylene Blue B, BB, and RR | 15. |
| New Methylene Blue F | 15. |
| *†Rhoduline Blue 5B | 3. |
| †Rhoduline Blue 6G conc. | 15. |
| Rhoduline Blue GO and 3GO | 15. |
| Rhoduline Sky Blue BB and 3G | 15. |
| †Turquoise Blue BB and G | 15. |
| Brilliant Rhoduline Blue R | 15. |
| *Green* | |
| †Methylene Green B | 15. |
| †Brilliant Green Crystals | 15. |
| †China Green Crystals | 15. |
| †New Green GI | 15. |

### *Acetane*

Acetane is a product of Weiler-ter Meer resembling Celloxan, used for the same purpose and in about the same manner. By adding acetane to the basic dye bath, deep shades are possible on acetate silks with certain basic dyes which otherwise are only applicable for light shades. Acetane has no detrimental effect upon the valuable properties of the acetate silk and in many instances deep shades may be obtained with only 1 or 2 per cent of dyestuff. It can be applied by Method No. 29, but by using the amount of Acetane shown in Table XXIV. The products starred are particularly fast to light.

TABLE XXIV

WEIGHT OF ACETANE TO BE USED WITH THE VARIOUS DYES ON ACETATE SILK

| *Name of Dye* | *Weight of Acetane in Ounces per Ten Gallons of Dye Bath* |
|---|---|
| Auramine | 16. |
| * Auramine O and II | 32. |
| Phosphine GG, GR and RE | 24. |
| Vitoline Pure Yellow 6G | 24. |
| Vitoline Yellow 5G, G, R and 2R | 24. |
| Vitoline Orange N | 24. |
| Chrysodine GG, G, 2GR and R | 24. |
| * Carthamine B, G and 6G | 24. |
| * Cerise B and G | 24. |
| * Magenta | 24. |
| Safranine G and N | 6.4 |
| * Crystal Violet | 8. |
| * Methyl Violet 10B, 5B, 2B, B, R, 3R and 5R | 16. |
| Red Violet | 24. |
| * Basilene Brilliant Blue 5B | 24. |
| Methylene Blue B, BG and M | 24. |
| Navy Blue B, R and 2R | 24. |
| Victoria Blue B and RBN | 24. |
| Sapphire Blue G, R and 3R | 24. |
| * Basilene Blue AZG and AZR | 24. |
| * Malachite Green | 24. |
| * China Green 4GN, G, 3G, G 2N and B | 24. |
| Methyl Green | 24. |
| * Brilliant Green | 24. |
| Bismark Brown 2G | 32. |
| Phenylene Brown 2G | 32. |
| New Grey | 32. |
| * Basilene Black AZ | 24. |

Bensancon[4] states that acetate silk is readily dyed with basic dyes after treatment with Kuhlmann's Acetonol N. Before dyeing, the fiber is immersed in an Acetonol N bath at 30 or 40° C. (86 or 104° F.) for 20 minutes. After centrifuging and washing, it is dyed with any of the common basic dyes without loss of luster or other desirable properties.

### *Topping with Basic Dyes*

The "mordanting" action of the acid dyestuffs for the basic dyes on various fibers is well known and widely used but it is not commonly known that this process may also be used to advantage on acetate silk. Even though the acid dye itself has only a slight affinity for the acetate silk, giving merely tints when used alone, it has a decided effect upon the depth of the shade obtainable with the basic dyes, as well as upon the exhaustion and fastness of the resulting color. In this manner it is also possible to apply basic dyestuffs which have no direct affinity for the acetate silk. This will be discussed more fully under the acid dyes. Also see the Setacyl and Setacyl Brilliant dyes, under Dyeing by Precipitation, Chapter XI.

### *Patents on Dyeing "Assistants"*

One of the first patents covering the use of salts in the basic dye bath was that of R. Clavel, British Patent No. 176,535, December 4, 1920. United States Patent No. 1,378,443, May 17, 1921, covers the same process. He states that the dye bath may contain one or more chlorides and an acid, with or without a protective colloid. Suitable chlorides are given as those of ammonium, potassium, sodium, barium, magnesium, zinc or tin (ous). Formic or acetic are suitable acids and the protective colloid may be gelatin, albumin, silk boil-off liquor, tannates, soaps, sulfonated fatty acids, etc. The dyeing is preferably effected in a foam bath as described in British Patents No. 102,310 and No. 103,638 which cover real silk dyeing. British Patents No. 187,964 (United States Patent No. 1,549,906), No. 199,754, and No. 204,179 cover similar processes. In a later patent, British Patent No. 182,830 (1922), Clavel states that magnesium chloride and stannous chloride in

the dye bath increases the affinity of the basic dyes for acetate silk. Also see British Patent No. 182,844; German Patent No. 355,533; and United States Patent No. 1,448,432, which cover the use of inorganic salts in the dye bath.

F. Bayer and Company obtained one of the first patents covering the use of organic compounds as assistants in the basic dye bath. Their British Patent No. 215,373, May 1, 1923, and United States Patent No. 1,517,581, December 2, 1924 (to P. Rabe), covers the use of pyridine and its homologues, such as methyl- or amino-pyridine in dye baths in connection with basic dyes. For example, a kilogram of Diamond Fuchsine (Magenta or Fuchsine) is dissolved in 1000 liters of water, to which 10 kilograms of pyridine are added. The wet-out material is placed in the dye bath and the dyeing carried on at about 60 to 70° C. (140 to 157° F.) for a half hour, after which any pyridine adhering to the fibers is removed by washing in dilute acetic or formic acid.

According to British Patent No. 215,783, May 9, 1924, to Carpmael and Ransford (Bayer and Company), acetate silk may be dyed in the presence of hydrogenated pyridine (piperidine), or a urea, or a derivative thereof, except the salts. For instance, guanidine, creatinine, or other aliphatic bases, or a compound of which these bases form a part, may be used instead of pyridine itself as described in British Patent No. 215,373 and United States Patent No. 1,517,581. For example, 5 kilograms of acetate silk may be dyed in a 100 liter dye bath containing 100 grams of Magenta and 1000 grams of piperidine or guanidine, at 60°C. (140° F.) for 30 or 45 minutes. The dyed material should be rinsed and acidified in the cold. The above patents were superseded by British Patent No. 216,838.

British Patent No. 216,838, May 28, 1923, to F. Bayer and Company possibly covers products such as Celloxan and Acetane. This patent states that in dyeing acetate silk (or other cellulose esters or their transformation products), a salt of an oxyacid of nitrogen or chlorine may be added to the dye bath in order to obtain deeper shades without using protective colloids. For instance, aniline nitrate may be used with Chrysoidine G; or sodium nitrate with Crystal Violet P. Nitrates of ammonia, sodium, magnesium, calcium and zinc, or of organic bases such as mon-

omethylaniline, guanidine, pyridine, or piperidine may be used, as may also their chlorates. Methylene Blue, Rhoduline Red B, Safranine, Auramine, and Bismark Brown are given as suitable dyes for application by this process.

As an example, this patent states that 1 part of Chrysoidine G may be dissolved in 1000 parts of water and 5 parts of aniline nitrate added. The dye bath should be in the proportion of about 20 to 1, at a temperature of 70° C. (158° F.), and the material dyed for at least one-half hour. Other inorganic and organic nitrates are mentioned, and in another example it is suggested to use 5 parts of sodium nitrate in place of the aniline nitrate, with the same quantity of dyestuff and water. A chlorate may be substituted for the nitrate.

R. Metzger in United States Patent No. 1,532,427, April 7, 1925, and J. Y. Johnson in British Patent No. 240,514, June 2, 1924 (Badische Company), states that the glyceryl acetate or other organic acid esters are frequently added to cellulose esters during manufacture in order to render the artificial silk more susceptible to dyeing.[b] Such compounds have also been used in the dye bath but are liable to attack or even destroy the fiber. In order to avoid this deleterious action and at the same time increase the affinity of the acetate silk for dyestuffs, he suggests treating the fiber with a solution of an ester of a mineral oxygen acid, especially salts of acid esters of a mineral oxygen acid, such as acid esters of sulfuric, phosphoric, or boric acid. The treatment with these esters or ester salts may be given in a bath previous to dyeing or the compound may be added to the dye bath, treating at either ordinary temperature for a considerable time or a higher temperature for a shorter time.

For example: 10 kilograms of acetate silk may be treated for about ten minutes at 50 to 60° C. (122 to 140° F.) with 300 liters of a 50 per cent by weight, solution of potassium ethyl sulfate containing a little acetic acid. The treated acetate silk is hydroextracted, stretched, and dyed without rinsing at 40 to 70° C. (104 to 158° F.) with one per cent of Diamond Green B in a bath slightly acidulated with acetic acid.

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[b]See German Patent No. 228,867.

According to the same patent, 10 kilograms of acetate silk may be entered into a 200 liter dye bath at 40° C. (104° F.) containing 100 grams of Auramine III, a little acetic acid and 6 kilograms of a 30 per cent aqueous solution of sodium dicresyl phosphate.

In the same manner, 1 kilogram of acetate silk may be worked for 10 minutes in 30 liters of a 5 or 6 per cent aqueous solution of sodium dicresyl phosphate, either at ordinary or an elevated temperature. It is then wrung out, stretched and dyed with 0.8 per cent of Methyl Violet 2B Extra at from 40 to 70° C. (104 to 158° F.), with or without the addition of purified waste sulfite cellulose liquor. Or the pretreated fiber may be dyed with 1 per cent of Azoflavine RS in a dye bath slightly acidified with acetic acid, in place of the Methyl Violet.

If preferred, 1 kilogram of the acetate silk may be treated at 40 to 50° C. (104 to 122° F.) with 30 liters of a 10 per cent solution of sodium dicresyl phosphate, wrung out and dyed at 40° C. (104° F.) with 10 per cent of Indanthrene Blue GCD paste (C. I. No. 1113), with or without the addition of a protective colloid, in a dye bath of which each liter contains three cubic centimeters of 40° Be. sodium hydroxide solution, 2 grams of sodium hydrosulfite powder and 10 grams of Glauber's salt. Also see British Patent No. 244,143.

According to Haerry[5] very good results along the same line as that obtained by means of Celloxan and Acetane, that is a better exhaustion of the dye bath, and an increased fastness with basic dyes, may be obtained by using certain soluble zinc salts, such as zinc chloride, nitrate, or preferably the acetate, in the basic dye bath. He compares the action of these salts to the "salting out" action of sodium chloride or sulfate in the application of the direct dyes to cotton; however, he may be in error on this theory. In some cases the zinc salt precipitates the basic dyestuff directly, in which case considerable care must be exercised in its use and the presence of acetic acid in the dye bath may be advantageous. The zinc salt should be added only in solution. He states that the action of the zinc salt is particularly noticeable in the case of basic dyes which do not exhaust well or give deep shades on acetate silk alone, such as Magenta, Victoria Blue, Phosphine, Auramine, etc., in which case the zinc may double the depth of shade with a con-

sequent saving where a standing dye bath is not used. Furthermore it will shorten the time of dyeing and allow lower temperatures to be used in the dye bath, both of which are an advantage when working with acetate silk. It also increases the fastness to rubbing, but in case this is not sufficient the dyed acetate silk may be rinsed for 15 minutes at 80° C. (176° F.) in water containing about 2 per cent of acetic acid.

*Method No. 30: Applying the Basic Dyes with Zinc Salts.* For light shades, prepare the 15 or 20 to 1 dye bath with about half the required amount of dyestuff and a little acetic acid. For dark shades the dye may all be added at the start. Enter the skeins luke warm and after working a few times remove them and add the remainder of the dyestuff in solution. Immerse the skeins again and slowly raise the temperature to 50° C. (122° F.). Continue working at this temperature until very little more color is going on the fiber and then start adding the zinc salt (in solution) in small portions, gradually raising the temperature to 55 or 66° C. (130 to 150° F.). The amount of the zinc salt varies with the particular dyestuff used and is best determined by experiment. It has been stated that the presence of acetin or glucose in the dye bath aids in leveling.

It is interesting to note that British Patent No. 247,694 to E. Knecht and F. Muller covers the use of water soluble compounds of magnesium and zinc in the application of the direct cotton dyes to cotton, in order to obtain colors which are faster to washing.

### *Dyeing Acetate Silk with Ammonium Thiocyanate*

Among other special methods of applying the basic, as well as other dyes to acetate silk, the British Cellulose and Chemical Company in British Patent No. 158,340, October 31, 1919; and Briggs and Palmer in United States Patent No. 1,398,357 November 29, 1922, suggest treating the acetate silk, either before or during the dyeing, with ammonium thiocyanate in solution in order to increase its affinity for basic, acid, direct, vat and other dyestuffs. Sodium, potassium or calcium thiocyanate may be substituted for the ammonium salt.[c] Methyl Violet, Coomassie Acid

[c] Also see the use of thiocyanates under Mordanting.

Blue R, and Dianol Fast Red K are given as examples of the many products applicable by this method. Five to twenty-five per cent solutions of the salt, at various temperatures, are applied for from two minutes to an hour or more.

These thiocyanates have a certain action on acetate silk which renders it more capable of absorbing and retaining basic, acid, direct, vat, and other dyes which alone have little or no affinity for acetate silk. However the results are not entirely satisfactory and the process has not come into general use. Too much thiocyanate will dull the luster of Celanese and possibly also of Lustron. Hall states that a microscopic examination of acetate silk treated with ammonium thiocyanate shows the surface to be crinkled. Wilson points out that the dyeing properties of viscose rayon are much increased when the surface is crinkled. Hanney suggests that thiocyanate has quite an action on cellulose itself at certain concentrations, and it is possible that the action on acetate silk may in some respects resemble the mercerization of cotton.

*Method No. 31: Dyeing Acetate Silk With the Aid of Ammonium Thiocyanate.* For example, the acetate silk may be treated for 15 minutes in a 25 per cent aqueous solution of ammonium thiocyanate, then washed in cold water and finally dyed in a bath containing 5 grams of Dianol Fast Red K per liter of water at 20° C. (68° F.). Many acid and direct dyes require only a 15 per cent solution of the thiocyanate. Another method is to dye the acetate silk for 15 minutes at 40 to 60° C. (104 to 140° F.) in a dye bath containing 1 kilogram of Naphthol Blueblack, 30 grams of Orange G and 24 kilograms of ammonium thiocyanate, per hundred liters. Vat dyes may be applied in a dye bath prepared with sodium hydroxide and hydrosulfite. In the case of Durindone Red B, the prepared vat is diluted with an equal volume of 3 per cent thiocyanate solution, and the acetate silk dyed at 20° C. (68° F.). Also see British Patent No. 244,143.

### *Basic Dyes on Saponified Acetate Silk*[d]

Of course the basic dyes may be applied to saponified acetate silk in the same manner as they are applied to cotton or the older

[d] See Chapter XIX.

rayons. Their affinity for the saponified fiber will vary in each case with the particular fiber to be dyed and the individual dyestuff used. In many cases where the basic dyes are to be used on the saponified fiber, it may be desirable to mordant the saponified acetate silk. This may be done in the same manner as given for mordanting cotton or the older rayons. British Patent No. 224,218 mentions that sulfurized phenols are applicable to saponified acetate silk as a mordant for the application of basic dyes.

### *Increasing the Fastness of Basic Colors on Acetate Silk*

*Method No. 32. Katanol After-Treatment to Increase Water Fastness of Basic Colors on Acetate Silk.* After dyeing and rinsing the acetate silk, but before drying it, enter it in a cold bath containing 3 to 6 per cent of Katanol and work it for 20 to 30 minutes. Rinse again and dry as usual.

*Method No. 33: Tannin Treatment for Increased Fastness to Washing.* In the same manner the fastness may be increased to washing by means of tannin and antimony, but with a dulling of the shade. The dyed and rinsed acetate silk is treated with 2 to 4 per cent of tannic acid for about an hour at 38° C. (100° F.) and then without rinsing, in a cold bath containing 1 to 2 per cent of tartar emetic for about 30 minutes. In many cases the fastness may be rendered satisfactorily by simply treating the dyed acetate silk in a single bath containing 0.5 per cent of tannic acid.

*Method No. 34: Copper Sulfate Treatment of Basic Dyes to Increase the Light Fastness.* The fastness to light of the basic dyes on acetate silk may in some cases be increased by rinsing the dyed acetate silk and then treating it in a bath containing 2 per cent of copper sulfate and a little acetic acid at 55 to 60° C. (130 to 140° F.) for 15 minutes. The shade is more or less dulled by this treatment. Also see British Patent No. 243,841, on a method of increasing the light fastness of colors.

In connection with the fastness of colors to light, it is interesting to note that Underwood[8] reports that the light fugitive colors are protected from this fading action to some exent by treating the dyed material with a dilute solution of phenol or resorcinol.

*The Gallocyanine Dyes on Acetate Silk*

The Gallocyanine dyes are of the basic mordant class and Clavel discovered that many of them could be applied directly to acetate silk. The Gallocyanine dyes have an affinity for acetate silk both by virtue of their basic function, due to the alkylamine groups, and the phenolic function of their gallic acid groups. They give violets, blues, and grays on acetate silk, many of which have good fastness to light and washing. Prune Pure,[6] also known as Violet PDH, is particularly fast and gives shades from lavender to rich navy blue. Modern Violet, Coreine RR, Gallamine Blue and Gallo Sky Blue are also useful.[7] Celestine Blue B gives good results but is not very level dyeing.

Many of these dyes are sensitive to metals and therefore copper dyeing vessels must not be used for their application unless ammonium thiocyanate is added to the dye bath. The dyestuff should be dissolved cold and the scoured wet fiber entered into the cold dye bath to prevent unevenness. Most of these dyes give brilliant shades but do not exhaust very well. The goods should be soaped after dyeing, and the colors may be fixed and developed by an after-treatment with bichromate and acetic acid as in Method No. 36. The Gallocyanine derivatives, such as Brilliant Alizarine Blue G, also dye acetate silk, provided they do not contain more than one sulfonic acid group. The addition of chromium acetate to the dye bath when applying the gallocyanine dyes will improve the fastness of some of them to washing. Methods No. 24 and 25 cover the application of both basic and gallocyanine dyes. They may also be applied by Method No. 35.

*Method No. 35: Gallocyanine Dyes on Acetate Silk.* Modern Violet, Gallocyanine, and Modern Heliotrope may be applied to acetate silk by entering the material into a cold dye bath and gradually raising the temperature. After dyeing, the shades should be soaped, and the ultimate shade developed and fixed by after-treatment in a chrome bath as in Method No. 36. Possibly certain other dyes of this class are also applicable by this method.

*Method No. 36: Developing and Fixing the Gallocyanine Dyes on Acetate Silk.* Enter the dyed and rinsed acetate silk into a fixing bath containing 1 to 2 per cent of bichromate and the same

amount of 40 per cent acetic acid. After working for some time, rinse the acetate silk well and dry at a low temperature.

It may also be well to note here that many of the free color bases of the basic colors, which are comparatively insoluble in water, may be applied to acetate in the form of aqueous suspensions by the dispersol method of application, which is discussed in Chapters XXI, XXII, and XXIII.

*References*

[1] R. G. Dort, *American Dyestuff Reporter 15*, 258-66 (1926).
[2] E. Greenhalgh, *Dyer and Calico Printer 55*, 106 (1926).
[3] J. Pokorny, *Rev. gen. mat. color, 29*, 224 (1926).
[4] J. Besancon, *Kunstseide 7*, 120-1 (1925).
[5] J. H. Haerry, "Artificial Silks."
[6] W. E. Sanderson, *J. Soc. Dyers and Colourists 38*, 162-5 (1922).
[7] J. F. Briggs, *J. Soc. Dyers and Colourists 37*, 287-96 (1921).
[8] H. W. Underwood, Jr., *Proc. Nat. Acad. Sci. 11*, 78-80 (1925).

# CHAPTER XI

# DYEING BY PRECIPITATION

*Applying the Basic and Other Dyes by Precipitation Methods and the Patents Covering This Process. The Setacyl and Setacyl Brilliant Dyes*

### *The Setacyl and Setacyl Brilliant Dyes*

WHILE the Setacyl dyes of the Geigy Company are very probably not all members of the basic group, at least some of them appear to belong to this classification; and their application by means of Setacyl Salt A, while possibly best described as a precipitation process, appears to resemble the application of the basic dyes by means of "assistants." It was previously stated that many organic compounds, such as dyestuffs, have a greater affinity for acetate silk when in a relatively coarse dispersion in the dye bath, as in the dispersol method of dyeing, than when in a higher state of molecular dispersion (or solution) such as in the ordinary dye bath. Very probably the increased affinity of the Setacyl dyes for acetate silk in the presence of Setacyl Salt A is due to the decreased solubility of the compound formed in water and the increased affinity for, or solubility of the new compound in, acetate silk.

The Setacyl and Setacyl Brilliant dyes are both entirely separate and distinct from the Setacyl Direct dyes which will be discussed with the acid dyes.[a] Very probably there is considerable difference in the composition of the brands of dyes now under discussion. Probably the Setacyl dyes are a group of specially selected basic, acid, and mordant dyes, while the Setacyl Brilliant dyes appear to be new products, regarding the composition of which very little appears to be known at present. The two groups are applied with Setacyl Salt A in an entirely different manner from that used for the Setacyl Direct dyes.

[a] See Chapter XIII

# CHAPTER XI

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[a] See Chapter XIII

The Setacyl and Setacyl Brilliant dyes are applied to acetate silk at low temperatures from a bath only slightly acid with acetic acid, and therefore the valuable properties of the acetate silk are not impaired in any way. They give very pure, bright and bloomy shades, and their fastness properties meet the usual requirements. However, they will not withstand cross-dyeing and usually stain other fibers present in the dye bath. In Table XXV which follows, the dyes starred possess a good fastness to light. In order to obtain the desired results, it is essential that the dyeing instructions, as given in Method No. 37, be followed closely.

*Method No. 37: The Setacyl and Setacyl Brilliant Dyes on Acetate Silk.* About a 30 to 1 dye bath should be prepared with the necessary quantity of dyestuff, calculated on the weight of the goods, and with gelatin or glue, as given in Table XXV, based upon the volume of dye bath in liters. The dyestuff should be dissolved in acetic acid before adding it to the dye bath, using a volume of acid in cubic centimeters equal to one-half of the weight of the dye in grams. Enter the previously thoroughly wet-out acetate silk at about 55° C. (131° F.), for light or medium shades, or at 65 to 70° C. (149 to 158° F.) for dark shades. Dye the goods for about 10 minutes, then remove the goods and add the first portion of Setacyl Salt A, as given in Table XXV, in solution. Mix well, re-enter the goods and dye for about 15 minutes. Add the second portion of Setacyl Salt A, always in solution, and continue the dyeing. After about 10 minutes more, the third portion of the Setacyl Salt A may be added, if necessary.

The whole dyeing operation usually requires about an hour for medium shades. Darker shades require a longer time, and black about 2 hours. After dyeing, the acetate silk should be rinsed and then soaped for 3 minutes in a cold bath containing 2 grams of soap per liter. This soaping is very important as it improves the fastness to rubbing. After soaping and brightening with formic acid, the material should be dried without previous rinsing at a temperature not exceeding 30 to 40° C. (86 to 104° F.)

## TABLE XXV

### Applying the Setacyl and Setacyl Brilliant Dyes With Setacyl Salt A

| *Formula No. and Color; Quantity and Name of Dye* | *Weight of Gelatin (in grams per liter of dye bath)* | *—Weight of Setacyl Salt A— (in grams per liter of dye bath)* 1st Addition (After 10 Minutes) | 2nd Addition (After Further 15 Minutes) | 3rd Addition (After Further 10 Minutes) |
|---|---|---|---|---|
| * 1—Lemon-Yellow: 2% Setacyl Yellow AO | 1.00 | 0.75 | 0.75 | .... |
| * 2—Orange: 2% Setacyl Yellow AO and 0.3% Setacyl Brilliant Pink G | 1.00 | 0.75 | 0.75 | .... |
| 3—Brownish-Orange: 2% Setacyl Orange CR and 1% Setacyl Yellow AO | 1.00 | 0.75 | 0.75 | .... |
| 4—Tan-Brown: 1% Setacyl Violet BR and 1% Setacyl Orange CR | 1.00 | 0.75 | 0.75 | .... |
| * 5—Tan-Brown: 2% Setacyl Violet BR and 1% Setacyl Yellow AO | 1.00 | 0.75 | 0.75 | .... |
| 6—Tan-Brown: 1% Setacyl Violet BR, 1% Setacyl Orange CR and 0.6% Setacyl Brilliant Pink G | 1.00 | 0.75 | 0.75 | .... |
| * 7—Cerese: 1% Setacyl Red FC | 2.00 | 0.20 | 0.40 | 0.40 |
| * 8—Eosine-Pink: 0.3% Setacyl Brilliant Pink G | 1.00 | 0.10 | .... | .... |
| * 9—Eosine-Pink: 2% Setacyl Brilliant Pink G | 1.00 | 0.75 | 0.75 | .... |
| *10—Scarlet: 4% Setacyl Brilliant Scarlet B | 1.00 | 0.75 | 0.75 | .... |
| *11—Scarlet: 2.5% Setacyl Brilliant Scarlet G | 1.00 | 0.75 | 0.75 | .... |
| *12—Scarlet: 4% Setacyl Brilliant Scarlet R | 1.00 | 0.75 | 0.75 | .... |
| *13—Greenish-Blue: 2% Setacyl Sky Blue S | 2.00 | 0.30 | 0.30 | 0.40 |
| *14—Greenish-Blue: 2% Setacyl Turquoise Blue S | 2.00 | 0.30 | 0.30 | 0.40 |
| *15—Bluish-Green: 2% Setacyl Green Bluish M | 1.00 | 0.75 | 0.75 | .... |
| *16—Deep Green: 2% Setacyl Green M | 1.00 | 0.50 | 0.50 | 0.50 |
| *17—Green: 2% Setacyl Green B | 2.00 | 0.40 | 0.30 | 0.30 |
| *18—Grass-Green: 1% Setacyl Green B and 1% Setacyl Yellow AO | 1.00 | 0.50 | 0.50 | 0.50 |
| *19—Sea-Green: 0.5% Setacyl Green M and 1.5% Setacyl Yellow AO | 1.00 | 0.50 | 0.50 | .... |
| *20—Greenish-Blue: 0.3% Setacyl Violet BR and 3% Setacyl Green M | 1.00 | 0.50 | 0.50 | .... |
| *21—Bluer Than No. 20: 0.75% Setacyl Violet BR and 2.25% Setacyl Green M | 1.50 | 0.50 | 0.50 | .... |
| *22—Blue: 1.6% Setacyl Violet BR and 2.4% Setacyl Green M | 1.50 | 0.75 | 0.75 | .... |
| *23—Violet-Blue: 1.6% Setacyl Violet BR and 2.4% Setacyl Green Bluish M | 1.50 | 0.75 | 0.75 | .... |
| *24—Dark Violet: 3% Setacyl Violet BR and 1% Setacyl Green Bluish M | 1.00 | 0.75 | 0.75 | .... |
| 25—Heliotrope: 1% Setacyl Violet MB | 2.00 | 0.30 | 0.30 | 0.40 |
| 26—Heliotrope: 1% Setacyl Violet MB and 0.3% Brilliant Pink G | 2.00 | 0.30 | 0.40 | 0.30 |
| 27—Deep Violet: 2% Setacyl Violet BR | 1.00 | 0.75 | 0.75 | .... |
| 28—Good Black: 8% Setacyl Black BN | 2.00 | 0.50 | 0.75 | 0.75 |
| 29—Good Black: 8% Setacyl Black GN | 2.00 | 0.50 | 0.75 | 0.75 |

*Patented Methods of Dyeing by Precipitation*

The first patent covering the application of dyestuffs to acetate silk by precipitation appears to be that of Ledward and Company, Harrison, and Burgess, British Patent No. 179,384, March 21, 1921. According to this patent the acetate silk is dyed with a colloidal dye solution prepared by adding to a solution of the dye, or its leuco compound, a protective colloid such as gelatin, casein, saponin, starch or their hydrolytic products; followed by a precipitant (except metallic chlorides), preferably a precipitant which is absorbed by acetate silk. Suitable precipitants are: for basic dyes, a weak alkali such as ammonia; a salt of an acid metallic oxide, such as molybdates, tungstates, or stannates; or an organic compound of acid character, such as tannic acid or salts of phenol, naphthols, aromatic acids, hydroxy acids, sulfonic acids, etc.; for acid or direct cotton dyes, a salt of an organic base such as aniline, benzidine, dianisidine, phenylenediamine, naphthylamine, etc.

Sulfur dyes are dissolved in sodium sulfide, hydrosulfite, etc., and the vat dyes in sodium hydrosulfite, the same precipitants being used as in the case of direct dyes. Mixed goods containing cotton may be dyed with sulfur or vat dyes as described above, the cotton threads being subsequently colored with direct dyes. The provisional specification describes the use of salts of ammonium, barium, magnesium, etc., as precipitants for direct and acid dyes, and of oxidizing agents, such as air or metallic salts, as precipitants for vat and sulfur dyes; it also refers to the use of alizarine dyes, using metallic salts, mordants, or organic substances as precipitants.

*Indigo on Acetate Silk*

For example, 100 grams of acetate silk are worked for five minutes in a bath containing 2 grams of indigo, 8 grams of caustic soda, 5 grams of sodium-hydrosulfite, 2 grams of glue, and 2 liters of water at 60 to 70° C. (140 to 157° F.). A solution of 0.5 gram of dianisidine in 4 cubic centimeters of glacial acetic acid and 200 cubic centimeters of water is then added in successive small quantities. The goods are removed from the dye bath and oxidized in the air. This process is more satisfactory for vat and

sulfur dyes than with the direct cotton dyes, as the latter are not fast to soap and alkalies when applied by this method.

*Basic and Direct Dyes by Precipitation*

The example given for basic dyes states that 100 grams of acetate silk may be dyed in a 2 liter bath containing 1 gram of Magenta, or 2 grams of Methylene Blue, and 2 grams of glue, raising the temperature to 70 or 80° C. (158 to 176° F.). A solution of 2 grams of sodium stannate in 200 cubic centimeters of water is then added gradually, while working the fiber. Saponin may replace the glue, and tannic acid the stannate. Diamine Sky Blue and other direct cotton dyes are applied in the same manner, only adding 0.5 gram of dianisidine base in 2 cubic centimeters of glacial acetic acid diluted with 200 cubic centimeters of water, in place of the sodium stannate solution.

British Patent No. 213,593, March 27, 1924, and French Patent No. 574,416 to J. R. Geigy very possibly covers Setacyl Salt A and the application of the Setacyl dyes. This patent supersedes British Patent No. 179,381. It states that acetate silk may be dyed by immersion at a temperature of 45 to 50° C. (113 to 122° F.) in an aqueous bath containing a dyestuff having little or no affinity for acetate silk, but which is precipitated by the addition of suitable aromatic substances, preferably in the presence of a protective colloid. Alternatively, the acetate silk may be previously treated with a solution of the precipitant, squeezed, and immersed in the solution of the dyestuff. Suitable precipitants include the sulfonic acids of benzene, naphthalene (*B*-naphthalene sulfonic acid) and anthraquinone, the salts of these acids and their hydroxy, alkyl, chloro, and nitro derivatives. Aromatic carboxylic acids, such as salicylic acid, may also be used as precipitants, and glue and gelatin as the colloid.

For example: acetate silk may be dyed by immersion in a dye bath containing 2 per cent of Methylene Green and 2 per cent of sodium diphenylaminesulfonate; or 2 per cent of Auramine O and 2 per cent of sodium *o*-cresotate; or 2 per cent of Martius Yellow, 4 per cent of gelatin and 2 per cent of benzoic acid; *B*-naphthalenesulfonic acid and gelatin with Magenta; or *B*-anthra-

quinonemonosulfonate and gelatin with Pyronine G, in a 60 to 1 dye bath.

British Patent No. 231,897, March 27, 1924, to J. R. Geigy, states that acetate silk may be printed with a paste containing aromatic sulfonic or carboxylic acids or their substitution products, or a salt of such an acid, and a dye which has only a slight affinity for this fiber. Protective colloids may also be included in the paste. By an alternative method, the acetate silk may be saturated with a solution of one of the acids mentioned, then dried and printed with the dye paste.

For example, 1 part of 2-napthol-7-sulfonic acid is dissolved in 13 parts of warm water and mixed with 36 parts of gum thickening. This is mixed with the color paste prepared from 1 part of Setoglaucine, 5 parts of 80 per cent acetic acid, 10 parts of water, and 34 parts of gum thickening. The prints are steamed and washed. Other suitable acids are the sulfonic acids of benzene, naphthalene or anthraquinone, salicylic acid and the hydroxy, alkyl, chloro, and nitro derivatives of these acids.

## CHAPTER XII

## MORDANTING ACETATE SILK

It is well known that the usual mordants, such as tannin and the common soluble salts of iron, aluminum, and chromium are not applicable to acetate silk as bottoming mordants, by the usual methods. However, as mentioned in Chapters X and XI, certain other inorganic and organic compounds are used as assistants in dyeing for certain effects. Recently several methods of mordanting this fiber by means of special salts, not ordinarily used as mordants, have been patented and may have a certain field of usefulness for various purposes.

French Patent No. 563,785, which was issued recently, states that when acetate silk has been treated with certain metallic salts, it has a greater affinity for dyes and that they penetrate better. Various tin salts, especially the chloride and bichloride, are recommended.

*Method No. 38: Mordanting Acetate Silk with Tin.* For example, one hundred grams of acetate silk may be treated in a bath containing 800 cubic centimeters of 20° Be. (1.16 sp. gr.) tin bichloride solution. After washing with water, it is treated with a 2° Be. (1.014 sp. gr.) sodium silicate solution. A second treatment at 40° C. (104° F.) is then given and the fabric washed. This treatment is claimed to have no detrimental effect on the acetate silk.

*Method No. 39: Mordanting Acetate Silk With Aluminum.* The Lustron Company[2] states that Lustron may be mordanted with aluminum by treating it overnight in a solution containing 8 parts of 8 to 10 Tw. (1.04 to 1.05 sp. gr.) aluminum acetate and 2 parts of glacial acetic acid. In the morning it should be hydroextracted, rinsed lightly once, and then dyed with alizarine or other suitable mordant dyes. A final treatment of the dyed acetate silk, consisting of Turkey-red oil, soda, and ammonia, is recommended.

The most recent patent along this line appears to be that of the British Dyestuffs Corporation, L. G. Lawrie and H. Blackshaw, British Patent No. 240,293, September 23, 1924. This states that acetate silk is capable of absorbing certain metallic mordants such as chromium, aluminum, or iron (ous), from their aqueous solutions provided the metal is present as a thiocyanate, benzoate, salicylate, phthalate, or other aromatic carboxylate or hydrocarboxylate, and may then be dyed by means of an appropriate dyestuff. Acids, alkalies, or other assistants can be used to assist the absorption of the salts by the acetate silk.

*Method No. 40: Mordanting Acetate Silk by Organic Salts of the Metals.* For example, the acetate silk may be treated for an hour at 75° C. (167° F.) in a 15° Tw. (1.075 sp. gr.) solution of aluminum thiocyanate. It is then treated for 5 minutes at 35° C. (95° F.) with a 1 per cent solution of sodium carbonate, rinsed, and dyed in a bath containing 7.5 per cent of 20 per cent Alizarine IP 20 per cent paste and 0.5 per cent of chalk, for an hour at 75° C. The dyed fabric should be soaped. The resulting bright red color is the same as the usual aluminum lake of alizarin. By similar methods a pale lilac shade may be obtained with chromium thiocyanate and Anthracene Blue BDG (C. I. No. 1059); a black color with iron thiocyanate and Haematine; or a bluish-violet color with chromium salicylate and Chromazol Violet (C. I. No. 892). Obviously many other combinations of mordants and dyes may be made to give a wide variety of fast colors of good depth of shade. Possibly the method may also be useful in increasing the fastness of the mordant dyes which have an affinity for this fiber. In this case the color could be top-mordanted. Davies[1] states that the process is not very successful on a commercial scale.

British Patent No. 215,012, April 26, 1924, to the Société Alsacienne de Produits Chimique covers the production of sulfurized phenols, completely soluble in aqueous solutions of sodium carbonate and suitable for use as mordants for basic dyestuffs, by heating a mixture of phenol, sulfur, and a small proportion of iodine, the last named acting as a catalyst. For example, 188 grams of phenol, 107 grams of sulfur and a small amount of iodine

are heated at 190° C., then at 210° C. for 4 or 5 hours, or until the evolution of hydrogen sulfide ceases. The viscous product is then cooled and powdered.

British Patent No. 224,218, October 18, 1924, to the same company, an addition to patent No. 215,012, covers the use of sulfurized phenol, its derivatives, or substitution products, as described in the previous patent, in place of tannin, for mordanting rayon. With basic dyes the colors obtained are nearly the same as on a tannin antimony mordant, and treatment with antimony is not necessary. The mordanting operation may take place in the same bath and concurrently with the application of direct or sulfur dyes, which are to be topped with basic dyes. In an example, acetate silk is treated in a bath containing the mordant, sodium hydroxide, and sodium phosphate, washed and dyed with a basic dye. From this example it would appear that this mordant is more applicable to the saponified acetate silk than the normal fiber.

Roetel[3] mentions a Badische "Mordant for Acetate Silk" about which little appears to be known in America. Also see Mordant LB in Chapter XIX, on the saponification process.

*References*

[1] H. R. Davies, *American Dyestuff Reporter 15,* 199 (1926).
[2] Lustron Company, "Recommendations for Finishing and Dyeing Fabrics Containing Lustron Silk."
[3] B. Roetel, *Textilber.* Jan. 1926; translation *American Dyestuff Reporter 15,* 387-8 (1926).

# CHAPTER XIII

## THE ACID AND MORDANT DYES ON ACETATE SILK

*The Setacyl Direct, Cellit Fast, Cellutyl, and Acetate Dyes*

THE classification of the older types of dyes for use upon cotton, wool, and true silk is not usually difficult, but with the advent of acetate silk a new factor entered upon this classification. Many of our older "acid" dyes are applied as "direct" dyes to acetate silk, while the bulk of the older acid and direct dyes have no affinity at all for the unhydrolyzed acetate silk. In the same way, many of the older mordant dyes also have a direct affinity for acetate silk and may be applied to it by methods similar to those used in applying the older direct dyes to cotton and the older rayons.

Now come along many of the new dyestuffs, the products of research upon acetate silk, and produced particularly for use upon it. Many of these new products are azo compounds containing acid groups, which, under the older methods of classifying the dyestuffs, would certainly be classed as acid dyes, yet they are applied to acetate silk by "direct" methods or the dispersol process.[a] Some few of these new azo dyes also have a slight affinity for cotton, but possibly none of them would come under the older classification of direct cotton azo dyes. Others of the new products, especially the anthraquinone compounds, resemble dyes of the older acid mordant and mordant classifications, such as some of the Acid Alizarine dyes. These, too, are sometimes applied by direct and dispersol methods to acetate silk.

From this it appears that the dyes which have an affinity for acetate silk will have to have a new and separate classification when used upon this fiber. Perhaps the first step in this line was the entirely new classification known as the dispersol dyes. However if we adhere to the older classification of acid and mordant dyestuffs, but include in it the new azo and anthraquinone products which are applied by direct methods, and which appear to fall

[a] See Chapters XXI, XXII, and XXIII.

within this scope, we have a very large, important, and rapidly growing group of dyes applicable to acetate silk by very simple methods, with excellent results.

The announcement of the dispersol type of dyes for acetate silk created considerable comment in the textile and dye field, which was certainly well deserved on account of their unique originality. While many of the new products which are here classified as acid and mordant dyes are just as useful in dyeing acetate silk as the dispersol dyes, they have not created nearly as much comment in the trade, because their theory and method of application is not entirely new. Many of these products have appeared upon the market recently, and undoubtedly some of them will eventually find a wide usefulness upon this fiber.

As discussed in Chapter VIII, acetate silk has no affinity for most of the older acid dyes, but some of them, particularly those which do not contain sulfonic acid groups, or only one sulfonic group, which may be counteracted by the presence of other groups, are applicable. While acetate silk has no affinity for the usual mordants, such as the common salts of iron, chromium, and aluminum, many mordant dyes may be applied to it without a mordant by virtue of their phenolic and ketonic functions. Where a mordant is desired for any particular reason, it may be applied as in Chapter XII. In using mordants on acetate silk it should be remembered that the color produced by most mordant dyes usually varies somewhat with the particular mordant used and even more when it is applied without a mordant.

It is well known that the sulfonic acid radicle confers solubility in water to many otherwise insoluble dyes and other organic compounds. At the same time, the sulfonic group decreases the solubility of the sulfonated compound in organic solvents. It has been pointed out by several investigators that the dyeing of acetate silk in many ways appears to resemble a solution phenomenon, such as the solution of the dye in an organic solvent; as, for instance, a hydrocarbon oil. Therefore we can readily see why the sulfonic acid group is not always desirable in dyes for this fiber. On the other hand, carboxylic acid groups also confer solubility in water upon many organic compounds, including dyes, without at the

same time so materially reducing the solubility of the carboxylated compound in organic solvents or acetate silk. At the present time it is impossible to classify all of the various new acetate silk dyes, but it is highly probable that some of the new products in powder form, as, for instance, the Setacyl Direct dyes, may be carboxylated aminoazo compounds.

The extent to which the sulfonic group or groups affect the solubility of the sulfonated compound in acetate silk, and possibly other organic solvents, depends not only upon the number of sulfonic groups present, but also upon their orientation, as well as the other radicles present in the molecule.[b] For this reason it is possible to apply certain monosulfonated dyes to acetate silk, which possibly most nearly resemble acid or mordant dyes in composition.

Some of the simpler anthraquinone derivatives, such as those of the alizarine series of dyes, are solubilized by sulfonating either the anthraquinone nucleus or attached arylamino groups. This principle is possibly used in the production of certain acetate silk dyes. However, when the more complex anthraquinone derivatives, such as the vat dyes are sulfonated, their solubility is decreased instead of increased. The carboxylic acid and certain basic groups which have been used in solubilizing some other classes of dyes are of little use in solubilizing the more complex anthraquinone derivatives. Indanthrene Blue WB (C.I. No. 1093) is a sulfonated anthraquinone vat dye which is somewhat soluble in hot water. While some of the dyestuffs used in the preparation of the dispersol type of paste dyes may be either sulfonated or unsulfonated azo compounds, the former resembling acid dyes in constitution, the more soluble anthraquinone compounds more nearly resemble the mordant dyes, and the comparatively insoluble products often approximate the vat dyes in constitution.

Perhaps the greatest advantages of the acid and mordant dyes over the basic dyes on acetate silk are their greater fastness to light and better leveling properties. As explained before, the affinity of the basic dyes for acetate silk possibly resides in the sul-

[b] See British Patent No. 226,948.

fate and acetate groups of the cellulose acetate molecule, and therefore any irregularity in the chemical constitution of the acetate silk, due either to acetylation or hydrolysis, renders it impossible to secure level shades with some basic dyes, while the trouble is even more aggravated with many of the special acetate silk dyes. Usually the acid and mordant dyes are not so sensitive in this respect, and therefore it is sometimes possible to obtain level shades on damaged or inferior goods with them. Usually the older acid dyes do not have sufficient affinity to give heavy shades on acetate silk, but this does not apply at all to the new dyes of this type prepared especially for acetate silk.

It is interesting to note, as mentioned in Chapter VIII, that in some cases the free color acid of the acid dye dyes the acetate silk a deeper shade than the sodium salt of the dyestuff, as in the case of Eosine I, Toluylene Orange, Acid Ponceau, etc. This only occurs when the free color acid is less soluble in water than its sodium salt. In the same chapter it was also mentioned that in some cases the affinity of the acetate silk for the basic portion of certain dyes, usually amino compounds, is sufficient to cause a partial decomposition of the dyestuff molecule, the basic portion entering the acetate silk.

While all dyes of the acid and mordant classification which have an affinity for acetate silk are very easy to apply to this fiber, the older members of this group have been almost wholly displaced for use on acetate silk by the newer members prepared especially for use on this fiber, and the Ionamine and dispersol type of dyes. These new dyes, while still retaining the ease of application of the older and better known acid and mordant dyes, offer many other advantages, such as deeper shades, a wider range of colors of greater fastness and brilliancy, etc., so that there is at present no reason to continue the use of the older dyes, which were really only makeshifts on acetate silk, except for special purposes. However, as the acid and mordant dyes are used on many other fibers in combination with acetate silk, their properties in regards to acetate silk are highly important. Then, too, some members of this classification are still used in printing and discharge work, etc.

The dyes of this class which are applicable, whether of the older group or the new special dyes for acetate silk, are frequently applied to acetate silk in light shades from a bath containing only soft water and the dyestuff. A neutral salt, such as sodium chloride or sulfate, is usually added to the dye bath, where heavy shades are desired, in order to aid the exhaustion, the action in this case being just the reverse of that in the basic dye bath, where it acts as a retard. In fact many of the formulas which are used for the basic dyes on acetate silk are used for the acid dyes also. In this way Methods No. 24 to No. 27 given under the basic dyes in Chapter X are recommended for the application of the acid dyes. Probably Method No. 24 is more practical. Method No. 41, which resembles Method No. 27, is also suggested for the application of acid and mordant dyes, but may be used for the basic dyes.

*Method No. 41: Acid, Mordant, and Basic Dyes on Acetate Silk with Ammonium Salts.* Use a 20 to 1 dye bath containing 15 to 30 per cent of ammonium chloride, according to the amount of dye used, to accelerate the exhaustion of the acid or mordant dyestuff. Enter the goods at 40° C. (105° F.), add the ammonium salt and gradually raise the temperature to 71 to 74° C. (160 to 165° F.) for one hour. The dyed goods should be rinsed and soaped for 10 minutes at 25 to 30° C. (77 to 85° F.) in a bath containing 2 pounds of soap per 100 gallons of liquor. This method has been particularly recommended for dyeing cotton-acetate silk unions with acid or mordant and direct cotton dyes.

The "mordanting" effect of certain acid dyes for the basic dyes was mentioned in connection with the basic dyes and this is the basis of an increased usefulness of both acid and basic dyes on acetate silk. The resulting shades are frequently much faster to water and washing than either of the component colors alone. It is also useful in obtaining deeper shades with the basic dyes, which, of course, also means a better exhaustion of the dye bath. Method No. 44 covers such a topping process and Table XXVI gives a list of a few of the innumerable colors obtainable by this process.

*Azo Dyes*

The azo dyes include many acid, direct cotton, and mordant dyes, some of which may be applied to acetate silk, possibly due to the basic character of the azo group. As mentioned before, those containing sulfonic acid groups, such as Benzopurpurin 4B (C. I. No. 448), Chlorazol Black E extra and Diamine Black BH (C. I. No. 401), are not suitable. Fast Oil Orange I (benzeneazo-*B*-naphthol, C. I. No. 24) gives satisfactory shades on acetate silk. In the case of Metanil Yellow, Orange IV, Silk Ponceau G (C. I. No. 196, sodium salt of 5- and 8-sulfo-*B*-naphthaleneazo-*B*-naphthol), and Brilliant Orange G (C. I. No. 26, sodium salt of benzeneazo-*B*-naphthol-6-sulfonic acid), the adverse action of the sulfonic acid group is partially overcome.

Diazo dyes, such as Pyramidol Brown BG and Bismark Brown may be used, but the latter does not usually give very deep shades on acetate silk. Some sulfonated azo dyes, chiefly yellows, oranges, and reds, as for instance Roccelin, may be dyed directly on acetate silk. Clavel suggested the addition of a small quantity of aniline hydrochloride to the dye bath when applying the simple monoazo dyes. Some azo dyes which contain no sulfonic groups but which are slightly soluble in water, as for instance Terra Cotta RS and Azochromine (tetrahydroxyazobenzene, C. I. No. 95) and their equivalents, may be used. Azo Yellow I is fast to light and useful as a bottom color for emerald and jade greens when topped with basic green or blue. Alizarine Yellow 3G and Alizarine Orange R may be after-treated with chrome if desired.

Azochromine gives a brown color and there are other browns which give more or less fast shades when fixed by after-chroming, as in Method No. 36. Alliance Fast Brown 5G paste[2] has exceptional fastness to light and a good fastness to acids, alkalies, washing and rubbing. Brotherton's Metachrome dyes are useful.[5] Rose Pink CA58 belongs to this class, while Chromocitronine, Chromoxanthine (C. I. No. 40) and Chrome Deep Brown RR are also used. Azo Yellow Conc., Orange IV, Alizarine Direct Violet ER, Alizarine Direct Blue A and SE, and Acid Alizarine Gray B will stain the cotton in cotton-acetate silk unions to some extent.

A recent paper by Hall and Aische[1] gives some very interesting

information regarding the affinity of various azo dyes for acetate silk, as compared to cotton and wool, as well as some new suggestions regarding the solubilization of azo dyestuffs for use on acetate silk and other fibers. Hall and Aische point out the fact that most of the dispersol dyes should be applied in an alkaline bath, which is a very decided disadvantage where they are used in connection with acid dyes, as on acetate silk-wool unions, by the one-bath method. On account of the retarding action of the sulfonic groups, as well as the carboxylic-acid groups to a smaller extent, in dyes for acetate silk, they propose to utilize arsinic ($AsO(OH)_2$) and stibinic ($SbO(OH)_2$) acid groups to solubilize suitable azo dyes for application to acetate silk from an acid or neutral dye bath. They prepared the sodium salts of the sulfonic, carboxylic, arsinic and stibinic acids of *a*-naphtholazophenol, *B*-naphtholazophenol, phenolazophenol, and salicylic acid azophenol. Table XXVI gives the colors obtained upon acetate silk in both acid and alkaline solutions, as compared with wool and cotton.

From experiments upon the application of these dyes and upon the fastness to boiling water, boiling soap and ammonia solution, and light, they conclude that:

*a.* Acetate silk and cotton have but little, and wool considerable affinity for the azo compounds described. All of the colors on wool have approximately equally good fastness to boiling water but have little fastness to boiling soap. Azo compounds containing sulfonic, carboxylic, and arsinic acid groups have approximately equal fastness to light, whereas, azo compounds containing stibinic acid groups are considerably less fast.

*b.* Azo compounds containing stibinic acid groups have a greater affinity than those corresponding compounds containing arsinic acid groups for acetate silk, but these differences cannot be correlated to differences in the solubilities of the azo compounds in water.

*c.* Azo compounds containing *B*-naphthol have a greater affinity for acetate silk than those containing *a*-naphthol. This is supported by other unpublished work by Hall and Aische.

*d*. The differences shown in the affinities of phenylazophenol-4-stibinic acid and salicylic acid azophenol-4-stibinic acid agree with the general observation that acetate silk has a decreasing affinity for azo compounds containing carboxyl and hydroxyl groups.

*e*. The affinity of acetate silk for azo compounds containing sulfonic, arsinic, stibinic and carboxylic acid groups increase in the order named.

TABLE XXVI

COLORS OBTAINED ON ACETATE SILK, WOOL, AND SILK WITH VARIOUS AZO DYESTUFFS SOLUBILIZED BY SULFONIC CARBOXYLIC ARSINIC AND STIBINIC ACID GROUPS

| Dyestuff as Sodium Salt of | Wool | Cotton | *Color On* Acetate silk Alkaline | Acetate Silk Acid |
|---|---|---|---|---|
| *a*-Naptholazophenyl-4-sulfonic acid | Deep brown | Stained bluish pink | Stained pink | —— |
| *B*-Naphtholazophenol-4-sulfonic acid | Bright reddish-orange | Stained pink | Pale orange | —— |
| Phenylazophenyl-4-sulfonic acid | Bright yellow | Unstained | Unstained | —— |
| Salicylic acid azophenyl-4-sulfonic acid | Bright yellow | Unstained | Unstained | —— |
| *a*-Naphtholazophenyl-4-carboxylic acid | Yellowish-brown | Pale pink | Stained yellow | —— |
| *B*-Naphtholazophenyl-4-carboxylic acid | Bright scarlet | Pale orange | Pale orange | —— |
| Phenylazophenyl-4-carboxylic acid | Yellow | Unstained | Unstained | —— |
| Salicylic acid azophenyl-4-carboxylic acid | Dull yellow | Stained yellow | Unstained | —— |
| *a*-Naphtholazophenyl-4-arsinic acid | Dull yellowish-brown | Pale yellow | Unstained | Deep reddish yellow |
| *B*-Naphtholazophenyl-4-arsinic acid | Bright orange | Stained orange | Stained orange | Deep orange |
| Phenylazophenyl-4-arsinic acid | Pale yellow | Unstained | Unstained | Yellow |
| Salicylic acid azophenyl-4-arsinic acid | Dull yellow | Unstained | Unstained | Greenish-yellow |
| *a*-Naphtholazophenyl-4-stibinic acid | Reddish-brown | Pale pink | Pale orange | Stained brown |
| Naphtholazophenyl-4-stibinic acid | Yellowish-orange | Pale orange | Pale orange | Deep orange |
| Phenylazophenyl-4-stibinic acid | Yellow | Pale yellow | Pale yellow | Stained yellow |
| Salicylic acid azophenyl-4-stibinic acid | Yellow | Pale yellow | Unstained | Stained yellow |

## *Nitro Dyes*

Nitro dyes such as Picric Acid and Martius Yellow (salt of 2, 4-dinitro-*a*-naphthol, C. I. No. 9) may also be used on acetate silk, but the shades are not of much importance. As Naphthol Yellow S (salt of 2, 4-dinitro-*a*-naphthol-7-sulfonic acid, C. I. No. 10) is sulfonated, it cannot be used. Hall[3] states that the nitroso dyes, Gambine Y (*a*-nitroso-*B*-naphthol, C. I. No. 2) and Alsace Green N (dinitrosoresorcinol, C. I. No. 1), obtained by the action

of nitrous acid on *B*-naphthol or resorcinol, respectively, are absorbed by acetate silk but have little tinctorial power except as iron lakes, so that they are of little practical value.

Of the remaining older and better known acid and mordant dyes which are applicable to acetate silk, Alizarine Orange AO (nitroalizarine, C. I. No. 1033) is very useful, Alizarine Garnet (C. I. No. 168) is not much changed by soaping. Alizarine Green S,[5] and Alizarine Blue S and ABS (C. I. No. 1067) are also used, the former for gray, and the latter for a light fast reddish-blue. Emmons[4] states that true Alizarine may be dyed on acetate silk from a bath of pure water only. Khaki Yellow WN[2] (C. I. No. 36) gives shades of good fastness from a salt bath but acids weaken the shade. Alizarine Yellow WS is useful for gold shades and in combination with other acid dyeing colors. It has good fastness properties, particularly to light and is applied with salt and acetic acid. Orange IV (C. I. No. 143) is fast to light, alkalies, and rubbing but is sensitive to acids.

Metanil Yellow Y (C. I. No. 138) has a fastness similar to Orange IV and is applied from a salty dye bath. Anthracene Brown WL (C. I. No. 1035) is useful for olive yellows and is applied by means of salt and acetic acid, as in Methods No. 25. It has good fastness properties, particularly to light, but is dulled by alkalies. Alizandine Orange M paste (C. I. No. 40) is dyed with salt and has good fastness. Citronine Y Conc. gives bright golden yellows from a neutral salt dye bath. It has good fastness properties but becomes orange in the light. Cloth Reds are useful for fast pinks and may be applied with other neutral or acid dyeing colors. Acid Rhodamine 3R, Coomassie Fast Violet 10BP and Indian Yellow GA or Azo Yellow A5W (C. I. No. 146) are also used. They are applied with acetic acid or 10 to 15 per cent of salt, as in Method No. 25. Coomassie Fast Violet is only moderately fast to light and the Indian Yellow reddens in shade but is fast.

Azo Yellow Conc., Acid Alizarine Gray B, Amido Yellow E (C. I. No. 11). Alizarine Direct Blue A and SE, Orange IV, Alizarine Direct Violet ER and R (C. I. No. 1074), Autochrome Olive Brown G Conc., and Chrome Blue BMI Conc., are also ap-

plicable to acetate silk. The acid dyes of this group, as well as Acid Alizarine Gray B and Autochrome Olive Brown G are of good fastness to washing, and are fast to acid, with the exception of Orange IV and Autochrome Olive Brown G, which change shade temporarily. This also applies to Victoria Yellow O (C. I. No. 138) which gives a fine yellow fast to light on acetate silk. Alizarine Yellow 2GW (C. I. No. 36) and RW (C. I. No. 40) may also be applied to acetate without after-chroming but do not give full shades.

Orange II (C. I. No. 151), Brilliant Orange O (C. I. No. 63) and G, Silk Scarlet O (C. I. No. 193), and Fast Red O (C. I. No. 176), give fairly full shades on acetate silk but are not very fast to light. Amido Yellow E, Orange IV, Alizarine Direct Violet R and ER, Alizarine Direct Blue SE, Modern Violet, Violet PDH, Prune Pure, Indian Yellow, Alizarine Yellow 3G, and Alizarine Orange R, are particularly fast to light. The light fastness of Azo Yellow, Acid Alizarine Gray B and Autochrome Olive Brown B is good. Chrome Blue BMI is very fast to washing and light, but should not be used in large quantities in the same dye bath with other dyes. Chrome Orange R (*p*-nitrobenzeneazosalicylic acid, also known as Alizarine Yellow R and Alizarol Orange R), and Pontachrome Yellow 3R are also useful on Lustron. Certain basic dyes such as Victoria Green WB and Methylene Green B may be used in the same bath with many chrome dyes. Topping certain of the acid dyes with basic dyes may improve the fastness to water and washing in some instances.

The following acid and mordant dyes of the older classification may also be applied to acetate silk directly by Method No. 24:

*Yellow*

Azoflavine S
New Yellow
Citronine Y and G
Azo Yellow Conc., I and A5W
Victoria Yellow O
Alizarine Yellow GG, 3G, 2GW, R, RW, and WS
Terracotta RS
Tropaeoline G
Quinoline Yellow
Amido Yellow E
Fast Yellow G and GL
Fast Light Yellow G and 3G
Indian Yellow G, R, and GA
Anthracene Yellow C
Era Chrome Olive
Khaki Yellow WN
Metanil Yellow Y
Pontachrome Yellow 3R
Chromocitronine
Martius Yellow

*Orange*

Orange II, IV, RO, G, GG, and Extra
Golden Orange
Pontachrome Orange
Tropaeoline OO and OOO
Alizarol Orange R
Chrome Orange R
Brilliant Orange O, G, and M
Oxychrome Orange RW
Brilliant Orange M, O, and G
Monochrome Orange R paste
Alizarine Orange AK and R
Azo Orange AO
Alizandine Orange M paste
Chromoxanthine

*Red and Pink*

Cloth Red B and G
Rocelline
Cerasine
Acid Rhodamine 3R
Ponceau G and GR
Silk Scarlet O
Fast Red A and O
Xylidine Red
Alizarine Garnet
Acid Scarlet 4R
New Ponceau 4R
Azo Acid Cardinal
Fast Red A and A new
Rhodamine B
Eosine Crimson 2B
Alizarine Bordeaux paste
Archil Substitute
Alizarin Garnet
Rose Pink CA58
Cardinal Red J

*Violet*

Fast Violet DH (Gallocyanine dye)
Gallocyanine D (Gallocyanine dye)
Alizarine Direct Violet ER and R
Alizarine Cyanol Violet R
Alizarine Maroon
Brilliant Milling Violet S4B
Brilliant Chrome Violet 4BR
Chrome Violet G
Coomassie Fast Violet 10BP

*Blue*

Chrome Blue BMI Conc.
Soluble Blues
Celestine Blue
Brilliant Alizarine Blue G
Alizarine Blue S and ABS
Alizarine Direct Blue A and SE
Alizarine Brilliant Blue B
Alcaline Blue H5B
Induline 5B
Alizarine Brilliant Blue B
Anthracene Blue 2B and 2BR
Alizarine Cyanine AK

*Green*

Alizarine Green S
Alsace Green N
Gambine Y

*Brown*

Azo Brown
Metachrome Brown B
Autochrome Olive Brown G Conc.
Resorcinol Brown R
Anthracene Acid Brown B
Naphthalamine Brown
Fast Brown N
Oxychrome Brown GR Extra
Oxychrome Brown BG
Monochrome Brown G paste and H paste
Oxychrome Brown GR extra and BG
Alizadine Brown M
Anthracene Acid Brown B
Naphthalamine Brown
Solochrome Brown MO
Anthracene Brown WL
Azochromine
Alliance Fast Brown 5G paste
Chrome Deep Brown RR

*Gray and Black*

Acid Alizarine Gray B
Omega Chrome Black PV
Nigrosine B Crystals

*The Cellutyl Dyes*

A selected list of dyestuffs, possibly all well-known acid, mordant and basic dyes, which dye acetate silk are marketed by the Brit-

ish Dyestuffs Corporation under the Cellutyl brand. While these dyes, in common with all of the other older dyes belonging to the same classes, are not at present used on acetate silk to any great extent, they still find a limited use for special purposes, such as in discharge printing. This group of dyes includes (*a*) Cellutyl Yellow C, Cellutyl Fast Yellow AY and B, Cellutyl Fast Tangarine, Cellutyl Fast Orange G and R, Cellutyl Fast Golden Orange, (*b*) Cellutyl Bright Red, Cellutyl Fast Red D, Cellutyl Fast Lilac and 2B, and Cellutyl Sky Blue. The dyes given under group *a* stain cotton and other rayons either slightly or not at all. The *b* group stain cellulose more and possibly at least some of these belong to the basic class.

*Method No. 42: The Cellutyl Dyes on Acetate Silk.* Most of the Cellutyl and Cellutyl Fast dyes may be applied by the methods generally used for the direct dyes on cotton, that is in a bath containing about 20 or 30 per cent of sodium chloride, at about 85° C. (185° F.) for an hour or less. In some cases, probably where the dyestuff belongs to the basic class (Cellutyl Sky Blue) it is necessary to add about 2 per cent of acetic acid also. When dyeing cotton-acetate silk unions, the Cellutyl dyes are frequently applied in the same dye bath with the direct cotton dyes. In the case of Cellutyl Fast Blue, the dyestuff is applied with 1 to 5 per cent of acetic acid. It can be aftertreated in a fresh bath with 1 to 3 per cent of bichromate and 1 to 3 per cent of formic acid to give violet shades of excellent fastness.

### *The Acetate Dyes*

The Acetate dyes of Actien-Gesellschaft fur Anilin-Fabrikation are selected acid and mordant dyes which are applicable to acetate silk. Two to four per cent of these dyes, on the weight of the material, are required to give medium shades. The manufacturers recommend topping these colors on the fiber with basic dyes, as in Method No. 44. Table XXVII gives a list of the shades obtainable by this topping operation. Five Acetate dyes are marketed: Acetate Yellow R, Acetate Orange G, Acetate Brown O and R, and Acetate Red A. Their fastness to water and washing is up to the usual requirements, and their light fastness,

with the exception of Acetate Red A, is good. All Acetate dyes may be mixed in the same dye bath.

*Method No. 43: The Acetate Dyes on Acetate Silk.* These products should be applied in a 20 or 30 to 1 dye bath containing 10 to 15 per cent of Glauber's salt crystals and 4 to 6 per cent of 30 per cent acetic acid at 60 to 71° C. (140 to 160° F.) for an hour or less. This method applies to all Acetate dyes except Acetate Brown O, which must always be applied with only 15 to 20 per cent of Glauber's salt, without acid, either when dyed alone or in combinations. After dyeing, rinse well and dry at 49 to 60° C. (120 to 140° F.).

*Method No. 44: Topping the Acetate Dyes with Basic Dyes* Enter the dyed and rinsed acetate silk in a fresh 30 or 40 to 1 dye bath containing 1 or 2 per cent of 30 per cent acetic acid and dye at 60° C. (140° F.). After dyeing, rinse, brighten by soaping if necessary, hydroextract and dry at 49 to 60° C. (120 to 140° F.).

TABLE XXVII

COLORS OBTAINED WITH THE "ACETATE" DYES TOPPED WITH BASIC DYES

| *Formula* No. | *Color* | *Acetate Dye* | *Topped With* |
|---|---|---|---|
| 1 | Moss Rose | 1.5% Acetate Red A | 0.01% Rubine Small Crystals |
| 2 | Orange Pink | 1.2% Acetate Yellow R | 0.1% Rubine Small Crystals |
| 3 | Red | 0.3% Acetate Red A and 0.6% Acetate Brown O | 0.3% Rubine Small Crystals |
| 4 | Eglantine 0.2242 | 3.0% Acetate Red A | 1.5% Rubine Small Crystals |
| 5 | Muncio 0.7012 | 0.5% Acetate Red A and 0.2% Acetate Brown R | 0.3% Methyl Violet 6B |
| 6 | Reddish-Violet | 1.0% Acetate Red A and 0.2% Acetate Brown O | 0.5% Methyl Violet 6B |
| 7 | Mallow 0.2702 | 3.0% Acetate Red A | 1.0% Methyl Violet 4R |
| 8 | Greenish-Blue | 0.15% Acetate Red A | 0.3% Methylene Blue 2B New |
| 9 | Light Blue | 1.5% Acetate Red A | 0.2% Methylene Blue 2B New |
| 10 | Bluish-Gray | 3.0% Acetate Red A | 1.4% Ethyl Green Crystals |
| 11 | Bright Brown | 1.0% Acetate Orange G | 0.15% Methylene Blue 2B New |
| 12 | Green | 0.5% Acetate Brown O | 0.3% Malachite Green Crystals |
| 13 | Bright Grass Green | 2.0% Acetate Yellow R | 1.0% Methylene Blue 2B New |
| 14 | Grayish-Olive | 3.0% Acetate Brown R | 1.2% Methylene Blue 2B New |
| 15 | Steel Blue | 0.5% Acetate Brown O | 0.3% Methylene Blue 2B New |
| 16 | Butterfly 0.5311 | 1.0% Acetate Yellow R | 1.0% Methylene Gray B New |
| 17 | Olive | 2.0% Acetate Brown O | 2.0% Methylene Blue 2B New |
| 18 | Light Gray | 0.5% Acetate Orange G | 1.0% Methylene Gray B New |
| 19 | Tan | 1.0% Acetate Orange G | 1.0% Methylene Gray B New |
| 20 | Brown | 1.5% Acetate Brown O | 0.2% Methylene Gray B New |
| 21 | Brown | 2.0% Acetate Brown O | 0.2% Methylene Gray B New |
| 22 | Violet-Brown | 0.75% Acetate Brown O | 0.4% Crystal Violet 6B |
| 23 | Golden Glow 0.3006 | 2.0% Acetate Orange G | 0.1% Chrysoidine extra |

*The Setacyl Direct Dyes*

One of the most interesting and successful brands of dyes which possibly come under this classification are the Setacyl Direct dyes of the Geigy Company. These dyes are entirely different in every way from the Setacyl Brilliant dyes of the same company which were covered in Chapter XI. The Setacyl Direct dyes are in powder form and are directly soluble in boiling water, which of course renders their use somewhat more convenient than that of paste products. It has been stated that they are entirely different from any other dyestuffs now on the market but as yet very little has been divulged regarding their composition. It is possible that they may be carboxylated aminoazo compounds. They are applied to acetate silk in exactly the same manner as the direct dyes to cotton, that is in a neutral bath. As the usual acid dyes are applied in the same manner, this apparently supports the above speculation regarding their constitution. The fact that they do not appreciably stain cotton indicates that they are not of the direct cotton type.

A wide range of shades are available and as they are applied at low temperatures in a neutral bath, their application leaves the acetate silk entirely unaltered in every way. They have good fastness to washing and rubbing, and withstand cross-dyeing well, with only a slight staining of the cotton or viscose in some cases. They are recommended for use in the same dye bath with the Art Silk Colors CW, to produce multicolor or shot effects on acetate silk-cotton or -rayon unions at a very low dyeing cost.

The Setacyl Direct dyes have given excellent results in printing by the ordinary methods, both on acetate silk and unions containing it. While these dyes do not discharge white, the ground is usually sufficiently clear to give good colored discharges. Table XXVIII gives some data upon the fastness of the various Setacyl Direct dyes and at the same time serves as a list of the colors available. Method No. 45. covers their application to acetate silk and Method No. 106 to combinations of acetate silk with true silk.

*Method No. 45: Setacyl Direct Dyes on Acetate Silk.* In applying these dyes, use methods similar to those used in applying the direct dyes to cotton to leave true silk white. For instance, light

shades may be obtained without using salt in the dye bath, but heavier shades may require from 10 to 20 per cent of Glauber's salt. The goods should be entered at 38° C. (100° F.), the temperature raised to 82° C. (180° F.) in about 20 minutes, and the dyeing continued for about the same length of time at this temperature. For blacks, it is recommended to start dyeing at 60° C. (140° F.), slowly raise the temperature to 75° C. (168° F.), and run for as long as two hours. The temperature is a large factor in matching shades.

TABLE XXVIII

FASTNESS PROPERTIES OF THE SETACYL DIRECT COLORS

| | | *Fastness to* | |
|---|---|---|---|
| | *Washing* | *Water* | *Rubbing* |
| Setacyl Direct Blue G Powder | 3 | 2–3 | 5 |
| Setacyl Direct Blue R Powder | 4–5 | 4 | 5 |
| Setacyl Direct Yellow 2G Powder | 5 | 5 | 5 |
| Setacyl Direct Yellow GR Powder | 5 | 5 | 5 |
| Setacyl Direct Yellow R Powder | 4–5 | 2–3 | 4 |
| Setacyl Direct Yellow 2R Powder | 5 | 5 | 5 |
| Setacyl Direct Orange G Powder | 4 | 4 | 3–4 |
| Setacyl Direct Orange 2R Powder | 3–4 | 3–4 | 4 |
| Setacyl Direct Red B Powder | 3–4 | 3 | 4 |
| Setacyl Direct Red G Powder | 3–4 | 3–4 | 4 |
| Setacyl Direct Scarlet G Powder | 3–4 | 3–4 | 4 |
| Setacyl Direct Scarlet 2G Powder | 5 | 5 | 4 |
| Setacyl Direct Black B Powder | 3–4 | 2–3 | 5 |
| Setacyl Direct Black G Powder | 3–4 | 2–3 | 5 |
| Setacyl Direct Black R Powder | 3–4 | 2–3 | 5 |

Note: In the above table the figure 5 indicates the colors of the highest degree of fastness while the lower numbers indicate a lower degree of fastness. This is just the reverse of the Colour Index.

### *The Cellit Fast Dyes*

The Cellit dyes of Bayer and Company are possibly azo compounds of an acid character, such as those covered by British Patent No. 225,862. As they are in powder form, they have certain advantages in handling over the paste products. However, as they stain cotton, wool, and true silk to some extent, they are not so well suited for contrasting multicolored acetate silk effects on unions. They are generally applied to unions by Method No. 95. The following dyes are available at present: Cellit Fast Rubine B,

Cellit Fast Red B, Cellit Fast Blue R, Cellit Fast Violet 2R, Cellit Fast Yellow 2G, 2GN and R, Cellit Fast Brown G, and Cellit Fast Orange G. All of these products are of high tinctorial power, but the Violet 2R is particularly strong, one per cent giving a deep brilliant shade, while as much as five per cent of some of the other dyes may be required for deep shades.

On acetate silk, Cellit Fast Red B, Rubine B, Orange G, Blue R, Yellow R and 2GN have a good fastness to washing and are about equal to the Diazo Fast types on cotton, usually exceeding the Benzo Fast colors. Cellit Fast Violet 2R and Brown 2G are not as fast to washing as the others. Their fastness to light is usually good as compared with the Benzo Fast colors, but Cellit Fast Brown G, Blue R, and Violet 2R are not as good in this respect as the others. As a class they do not withstand cross-dyeing at the boil, but this is seldom necessary or desirable on acetate silk. They do not discharge to a clear white with sodium formaldehyde sulfoxylate. While they stain the cotton or viscose present in unions, this staining may be removed by a soaping, as explained under clearing unions. They dye both true silk and wool from an acid or neutral dye bath, acetic acid completely exhausting the dye bath, and may therefore have a particular usefulness for certain solid shades on wool or true silk acetate silk unions. Cellit Fast Yellow 2GN, which may be diazotized and developed on the fiber, is discussed further under the Developed Colors, Chapter XVII.

*Method No. 46: The Cellit Fast Dyes on Acetate Silk.* These dyes should be applied in about a 25 to 1 dye bath at 60 to 65° C. (140 to 150° F.) with an addition of 30 to 50 per cent of sodium chloride or anhydrous sulfate. In the case of Cellit Fast Yellow 2GN, a further addition of 3 to 5 per cent of 30 per cent acetic acid is required. Ordinarily they may be combined with each other, or with other dyes, for use in dyeing compound shades or unions.

*Method No. 47: Alkali Blue on Acetate Silk.* Alcaline Blue H5B (Alkali Blue) may be applied to acetate silk in a neutral salt bath at 60 to 70° C. (140 to 158° F.) for about an hour. The fiber should then be rinsed and the color developed at 40 to 60° C.

(104 to 140° F.) in a formic acid bath. In case acid dyes are used with this blue, they may be applied in the acid developing bath.

*Method No. 48: Alizarine Red on Lustron for Gold Color.* Alizarine Red Y and B, 20 per cent pastes, may be applied to Lustron to give either gold or purple shades (Method No. 49), depending upon how it is applied. For a gold shade, the dye bath is prepared with 4 per cent of Alizarine Red Y, 2 per cent of tannin, 1 per cent of acetic acid and 2 per cent of salt. The material is dyed at 80° C. (175° F.) for an hour. If the color is too glary it may be dulled or browned somewhat by substituting potassium bitartrate (cream of tartar) for the acetic acid above; or the dyed material may be after-treated in a cold bath containing a pound each of sodium carbonate and soap per 120 gallons of water, until the desired brown is obtained. Where this method is used in dyeing acetate silk-cotton unions, it may be necessary to clear the cotton with dilute acetic acid or a sodium bicarbonate and soap treatment, as described in Clearing Unions.

*Method No. 49: Purple on Lustron with Alizarine Red.* Use 2 per cent of Alizarine Red and just sufficient acetic acid to keep the dye bath an orange color, and not red, when hot. Dye for one hour at about 80° C. (175° F.) and then develop the color at the same temperature in a bath containing 5 per cent of Turkey-red oil (soda), slightly alkaline with ammonia. This treatment should be continued until the acetate silk comes to its final shade, or if this shade is obtained rather soon, for at least one-half hour, in order that the color shall be fully developed throughout the fiber and keep its shade on drying. This Turkey-red oil treatment will also usually clear the cotton in acetate silk-cotton unions.

*Method No. 50: Alizarine Violets and Browns on Lustron.* Alizarine Violet 2BS and Z4B, and Alizarine Browns, such as the ZW marks, may be applied to Lustron with a small amount of acetic acid, as in Method No. 25. The progress of the dyeing can be determined by spotting the goods with a little ammonia as the color does not develop in the acid bath. After dyeing, the goods should be rinsed and developed with Turkey-red oil and ammonia as in Method No. 49.

*Method No. 51: Alizarine Blue on Lustron.* Alizarine Blue S (C. I. No. 1067) may be applied to Lustron in a dye bath containing 2 to 4 per cent of the dyestuff, 1 per cent of acetic acid, 15 per cent of salt and 6 per cent of 32° Tw. (1.16 sp. gr.) chromium acetate liquor. Dye at not over 65° C. (150° F.) for an hour, rinse and steam for one hour without pressure. The color may be brightened by topping it with a mixture of Crystal Violet and Victoria Green in a neutral bath, which may be heated to aid the exhaustion. In using this method on acetate silk-cotton unions, the cotton should be cleared with sodium bicarbonate and soap, before the topping operation.

*Method No. 52: Anthracene Blue on Lustron.* Anthracene Blue can be applied as an acid dye with acetic acid and salt, as in Method No. 25, or it may be applied with salt alone, in which case the shade is bluer and weaker. In the latter case, on unions, it gives a lavender shade on the Lustron and a dull blue shade on the cotton. The fastness to light is excellent and good to acids, alkalies, washing, and rubbing.

The application of the acid dyes to acetate silk by means of ammonium thiocyanate is covered by Method No. 31, Chapter X.

*References*

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[2] W. E Sanderson, *J. Soc. Dyers and Colourists 38,* 162-5 (1922).
[3] A. J. Hall, *Textile Colorist 46,* 153-7 (1924).
[4] G. Emmons, *American Dyestuff Reporter 10,* 268 (1922).
[5] J. F. Briggs, *J. Soc. Dyers and Colourists 37,* 287-96 (1921).

# CHAPTER XIV

## THE PATENTS COVERING THE PREPARATION AND APPLICATION OF DYES OF THE ACID AND MORDANT TYPE TO ACETATE SILK

In any discussion of the patents covering the preparation and application of dyes for and to acetate silk, it is frequently almost impossible to positively classify the patent from the information available. Very often products which from the patent appear to be of the acid or mordant type, are applied by the dispersol method. In fact, without doubt many of the products covered in the following patents may be applied by either direct or the dispersol methods, which latter, after all, is really a direct method also, only that generally the dyestuffs used in the dispersol method are not very highly soluble in water and are therefore solubilized in the dye bath by a special method which will be discussed later. Also some of the products covered by these patents resemble vat dyes but are probably not applied by the alkaline hydrosulfite method. In some cases, patents given in connection with the dispersol dyes, Chapter XXIII, may belong in the present chapter. Many of the new acid and mordant dyes also have some uses upon fibers other than acetate silk, such as wool, or true silk.

One of the first patents covering the application of acid as well as other dyes to acetate silk is British Patent No. 158,340 and United States Patent No. 1,398,357, previously mentioned in Chapter X in connection with the use of ammonium thiocyanate in dyeing.

British Patent No. 190,313, October 29, 1921, to W. Harrison and Burgess, Ledward & Company, covers the use of dyestuffs containing an azo group associated with one or more alkylamino groups, but not containing sulfonic or carboxylic groups directly attached to the carbon atoms in the benzene nuclei. Suitable dyes are those prepared by coupling methylaniline or dimethylaniline with the diazo compounds of aniline, chloroanilines, nitro-

anilines, nitroanisidine, aminomethylanilines, aminodimethylaniline, naphthylamines or aminoazobenzenes, or with the tetrazo compounds of benzidine, dianisidine, or diaminodiphenylmethane. Such dyes are usually soluble in formic, acetic, or sulfuric acid, and may be mixed with water and a protective colloid. They are usually applied at 70 to 80° C. (158 to 176° F.) to give yellow, orange, or red shades. A provisional specification states that aminoazo compounds or arylaminoazo compounds, such as aminoazotoluene, aminoazonaphthalenes, aminoazonaphthols, or aminoazonaphthylamines, may also be used.

British Patent No. 202,157, July 29, 1922, to the British Dyestuffs Corporation, E. B. Anderson, J. Baddiley, and J. Hall; and United States Patent No. 1,498,315, June 17, 1924, to the last two inventors above, cover carboxylated azo dyes. These patents state that acetate silk may be dyed directly by means of aminoazo or aminoazo substituted dyes, solubilized by means of one or more carboxyl groups, in place of the usual sulfonic group or groups. These dyes may contain diazotizable amino groups, so that different shades may be obtained by diazotization and development on the fiber with the usual components, such as the naphthols, phenols, etc. The dyes are applied directly as their sodium salts in an aqueous dye bath, either alone or with sodium chloride, sulfate, or a dilute acid, to assist exhaustion. The resulting shades are similar to those of the corresponding Ionamines.

The following examples of acetate silk dyes are given with the colors obtained directly and by diazotization and development: When *m*-aminobenzoic acid with *o*-anisidine is dyed directly, a yellow color is obtained, which upon development with *B*-hydroxynaphthoic acid gives a magenta red color; or with *p*-aminodiphenylamine, a golden yellow color. *m*-Aminobenzoic acid with anthranilic acid gives a direct yellow color which with *B*-naphthol develops a red; with *B*-hydroxynaphthoic acid, a bluish-red; or with *p*-aminodiphenylamine, an olive color. *p*-Aminosalicylic acid with *a*-naphthylamine also gives a direct yellow, which with *B*-naphthol gives a violet; *B*-hydroxynaphthoic acid, a reddish-blue; or with *p*-aminodiphenylamine, an olive color.

5-Acetylamino-2-amino-4-methoxytoluene with *B*-hydroxynaph-

quinone dyes, which are very soluble in water, dilute acids, and alkalies may be prepared from a suitable aminoanthraquinone by condensation with an alkylene oxide carboxylic acid in glacial acetic acid, with or without a catalyst, such as copper. For example, 10 parts of 1,4-diaminoanthraquinone are suspended in 100 parts of glacial acetic acid and 0.5 part of copper acetate. Twenty parts of methylglycidic acid are added; and after stirring for two days at room temperature, the whole is poured into 2000 parts of water, the solution neutralized with sodium hydroxide, 100 parts of salt added, and filtered. The dyestuff is salted out from the filtrate and forms a blue powder on drying. The product dyes wool very bright shades of good general fastness, as well as dyeing acetate silk. The dyes obtained from methylglycidic acid or the potassium salt of phenylglycidic acid and 1,4-diaminoanthraquinone give blue shades; while the latter acid gives a red dye with $\alpha$-aminoanthraquinone; or, a purple dye with $\alpha$-amino-4-hydroxyanthraquinone.

Very probably the Cellit dyes are covered by British Patent No. 225,862, December 5, 1923, to F. Bayer and Company. This process covers the production of azo dyes by coupling diazotized dinitroanilinesulfonic or carboxylic acid with an aromatic amine, which does not contain a sulfonic group, but which may be substituted in the amino group. For instance, a deep red color may be obtained on acetate silk with the product obtained by diazotizing 280 parts of the ammonium salt of 2,6-dinitroaniline-4-sulfonic acid and coupling with 143 parts of $B$-naphthylamine in acid solution. The 2,6-dinitroaniline-4-sulfonic acid may also be coupled with $\alpha$-naphthylamine or ethyl-$\alpha$-naphthylamine. Other suitable dyes are obtained by coupling 2,4-dinitroaniline-6-sulfonic acid with ethyl-$B$-naphthylamine; or 2,4-dinitroaniline-6-carboxylic acid with ethyl-$B$-naphthylamine. These latter products dye acetate silk bordeaux, violet, blue, and bluish-violet shades, respectively. Also see German Patent No. 423,601.

British Patent No. 226,948, November 30, 1923, to the British Dyestuffs Corporation and G. H. Frank, covers the use of monosulfonated azo dyes which do not contain hydroxy groups, and have this sulfonate group in the ortho position to an azo group. Monoazo dyestuffs prepared by combining an unsulfonated diazo

compound, containing no hydroxy groups, with naphthylamino-8-sulfonic acid or its phenyl or other derivatives, also have an affinity for acetate silk. A hydroxyl group is capable of increasing the activity of the sulfo group to such an extent as to diminish the affinity of the dye for acetate silk.

In this manner acetate silk dyes may be obtained by coupling diazotized 2,1-naphthylaminosulfonic acid with *N*-alkyl or *N*-aryl substituted amines, particularly substituted naphthylamines, or with *m*-toluylenediamine. For instance, the products from diazotized *p*-nitroaniline-*o*-sulfonic acid combined with phenyl-*a*-naphthylamine (brown), *p*-tolyl-*a*-naphthylamine (brown), ethyl-*a*-naphthylamine (violet), ethyl-*B*-naphthylamine (violet), phenyl-*B*-naphthylamine (violet), *a*-*a*′-dinaphthylamine (brown), or *B*-*B*′-dinaphthylamine (bluish-violet), have a high affinity for acetate silk. By the reduction of the nitro group and coupling with a *m*-diamine, other valuable dyes are obtained. Other acetate silk dyes mentioned which contain sulfo groups in the peri position to the amino or substituted amino group, are *p*-nitroanilineazo-1, 8-naphthylaminesulfonic acid (peri acid) and *p*-nitroanilineazo-phenyl-peri acid. These dyes are applied to acetate silk from slightly alkaline dye baths. Also see United States Patent No. 1,534,506.

According to British Patent No. 228,557, January 29, 1924, to Meister, Lucius and Bruning, acetate silk may be dyed deep violet to blue shades of good fastness to washing and excellent fastness to light by monosulfonated 1, 4-diaminoanthraquinone or 1, 4-aminohydroxyanthraquinone, or an alkyl, aralkyl or aryl derivative of these compounds having the sulfo group in the 2- or 3-position. The dye bath may also contain salts, acids, or protective colloids. United States Patent No. 1,587,669, June 8, 1926, to C. E. Muller, assigned to the Grasselli Dyestuff Corporation, covers the same process.

British Patent No. 230,055 of 1925, a modification of patent No. 225,862, states that a blue dye for wool may be obtained by coupling diazotized dinitroanilinesulfonic or carboxylic acid with the sulfonic or carboxylic acid of *B*-naphthylamine or its derivatives.

British Patent No. 232,599, April 15, 1925, to Meister, Lucius and Bruning states that the glycines, obtained by the action of the halogen-acetic acids on nonsulfonated aromatic bases, including basic dyestuffs containing a free amino group, and particularly their water-soluble salts, are suitable for dyeing acetate silk by direct absorption. Acids, salts, or protective colloids may be added to the dye bath and the compounds may be diazotized on the fiber, and developed with an amine, phenol, or aminophenol. For example, a kilogram of acetate silk is dyed a fast violet shade by immersion for an hour at 60 to 70° C. (140 to 158° F.) in a 20 or 25 to 1 dye bath containing 20 grams of the glycine formed from 1,4-diaminoanthraquinone. Yellow, deep blue and reddish-violet shades are obtained by using the glycines formed from aminoazobenzene, 1,4,5,8-tetraaminoanthraquinone, and 1-amino-4-hydroxyanthraquinone respectively. A violet-black color of good general fastness properties is obtained by dyeing acetate silk with the glycine of *a*-naphthylamine, subsequently diazotizing on the fiber and coupling with *B*-hydroxynaphthoic acid.

British Patent No. 243,737, November 25, 1924, to Meister, Lucius, and Bruning, states that the slightly basic monoazo dyestuffs containing a sulfamino group in the diazo component are particularly suitable for dyeing acetate silk and other cellulose esters and ethers in deep, fast colors. For example, 1000 grams of acetate silk can be dyed in a 20 to 25 liter bath containing 30 grams of the dyestuff from diazotized 4-aminobenzene-1-sulfamide and aminocresol ether. The temperature is gradually raised to 70° C. (158° F.), maintained for a half hour, 200 grams of ammonium acetate are added and the dyeing continued at 70° C. for a further half hour. After rinsing, a vivid golden yellow color of excellent fastness is obtained. Diazotized 2-nitro-1-aminobenzene-4-sulfamide with *m*-toluidine gives an intense orange; and diazotized 4-aminobenzene-1-sulfamide with *a*-naphthylamine gives a deep reddish-orange. British Patent No. 243,738 is probably along the same line.

British Patent No. 244,267 of 1924, to the British Dyestuffs Corporation, W. H. Perkin and C. Hollins appears to cover a new variety of acetate silk direct dyestuffs. This patent states that

acetate silk may be dyed various shades directly by derivatives of amino-, diamino-, or polyamino-anthraquinones or their substitution products, excluding sulfonated derivatives obtained by complete acylation followed by nitration. The products may be hydrolyzed and reduced if desired. Other nonaromatic acyl groups may be introduced instead of the acyl groups, but it is found that benzoylation destroys the affinity for acetate silk. It is unnecessary to use a dispersing agent such as that referred to in British Patent No. 224,077 or other dispersing agents, such as Turkey-red oil. For example, 20 kilograms of diacetyl-1, 8-diaminoanthraquinone are dissolved in 100 kilograms of concentrated sulfuric acid and mononitrated at 5 to 10° C. with 48 liters of mixed acid, containing 200 grams of nitric acid per liter, for an hour. The product is precipitated by pouring into water, and may be crystallized from chlorobenzene. It gives a rich brown shade on acetate silk directly.

British Patent No. 245,758, January 6, 1925, to the Chemische Fabrik vorm. Sandoz covers the production of cellulose ester dyes, suitable for use on acetate silk, containing one or more glycol ether or glycerol ether groups in the aryl nuclei, but no sulfonic or carboxylic groups. They may be prepared by coupling diazotized aminoarylglycol ethers or aminoarylglycerol ethers with the usual components.

In British Patent No. 245,790, to the I. G. Farbenindustrie, the dyeing of cellulose esters and ethers with monoazo dyes containing as a coupling component an *o*-aminophenol ether or a monoacyl-*m*-phenylenediamine or a homologue or substitute thereof, is covered. The dyeings may be diazotized and developed. Examples are given for obtaining a deep yellow, an orange, and yellow to orange tints on acetate silk.

British Patent No. 248,858, December 16, 1924, to the British Dyestuffs Corporation, W. H. Perkin and C. Hollins, covers new carbamides of the anthraquinone series containing 2 or 3 anthraquinonyl groups linked together by the chain -NH.CO.NH-, which have an affinity for acetate silk. These are obtained by condensing $\alpha$-anthraquinonylethyl carbamate or $\alpha$-anthraquinonylcarbamic chloride with equimolecular proportions of $\alpha$-aminoanthraquinones or derivatives, preferably those having two amino groups in the

$\alpha$-positions, such as 1,4-, 1,5-, 1,8-diaminoanthraquinones, diaminoanthrarufin or diaminochrysazine. For example, 13.5 kilograms of diaminoanthrarufin when heated with 14.5 kilograms of $\alpha$-anthraquinonylethyl carbamate (or an equivalent porportion of the corresponding carbamic chloride) at the melting point of the mixture for about a half-hour, form a product which dyes acetate silk a brown shade and is probably a monocarbamide. Diaminochrysazin and $\alpha$-anthraquinonylethyl carbamate condensed in the same way give a product which is probably the dicarbamide and which dyes acetate silk a steel-gray shade. These products may possibly be applied by a dispersol method.

British Patent No. 252,240, November 25, 1924, to C. M. Barnard and the British Alizarine Company states that acetate silk and other cellulose esters may be dyed with compounds having the general formula $A.N.(Y.CO_2H)R_1$ or $A.N.(Y.CO_2H)Z.CO_2H$, in which A is an unsulfonated aryl dye nucleus, N is an atom of nitrogen, $R_1$ is an atom of hydrogen or an alkyl or other substituent, and Y and Z are the same or different aliphatic chains which may be branched or straight, substituted or unsubstituted. The nonsulfonated aryl dye nucleus may be any of the well-known groupings such as anthraquinone or its derivatives, azo compounds, indigo or its derivatives, but it is preferable to maintain the molecular weight as low as possible. One group of especially suitable compounds of this type is formed by the condensation of a molecule of amino- or imino-derivative of an unsulfonated aryl dye nucleus with at least one molecule of an aliphatic polycarboxylic acid. Two general methods for preparing suitable substituted glycine dyes are (*a*) treatment of one molecule of an aromatic amine in a suitable solvent with one molecule of an aldehyde, one molecule of sodium bisulfite, and one molecule of potassium cyanide, and subsequent hydrolysis with boiling sodium hydroxide or sulfuric acid of the nitrile thereby formed. (*b*) Condensation of an aromatic amine with a halogenated aliphatic acid other than halogenated acetic acid. The anthraquinone derivatives of this type give very bright and fast shades, chiefly orange and red. Thus, the condensation product of 1-aminoanthraquinone and *B*-chloropropionic acid, dyes red. The compounds prepared by fusing *o*-carboxyphenylamino-

diacetic acid with potassium hydroxide and oxidation of the leuco compound, dyes blue.

British Patent No. 252,646, November 15, 1924, and July 4, 1925, to Barnard and the British Alizarine Company states that acetate silk and other cellulose esters may be dyed by azo and anthraquinone compounds having the general formula A.X.Y. $CO_2H$, in which A is a nonsulfonated aryl dye nucleus, X is an atom of oxygen or sulfur, and Y is a straight or branched substituted or unsubstituted aliphatic chain. It is desirable that A has a low molecular weight but either azo or anthraquinone compounds are suitable. One group of such dyes consists of derivatives of glycollic or thioglycollic acid or homolgues of these acids in which a hydrogen atom attached to the oxygen or sulfur atom is replaced by an unsulfonated aryl dye nucleus. Suitable compounds are: (1) the azo dye prepared by condensing *p*-nitrophenol with chloroacetic acid, then reducing the nitro group to an amino group, and afterwards diazotizing and coupling with *B*-naphthol. (2) Anthraquinone and its derivatives are especially suitable as the aryl nuclei to be linked with the oxygen atom. (3) 1-Amino-anthraquinone-2-thioglycollic acid obtained by treating 1-amino-2-mercaptoanthraquinone with sodium hydroxide and glucose at 70° C. (158° F.) and adding chloroacetic acid, dyes orange-yellow. (4) By boiling 1-amino-2, 4-dibromoanthraquinone with sodium sulfide and then condensing with chloroacetic acid a dyestuff is obtained which dyes a bright bluish-red color. (5) 1- and 2-amino-anthraquinonethioglycollic acids are yellow dyes.

In British Patent No. 253,457, June 29, 1925, W. Carpmael for the Bayer Company, states that monoazo dyestuffs giving pure, even shades on wool are obtained by coupling diazotized amines or their substitution products with omega-aminoalkyl-*B*-naphthylamines or their derivatives prepared as in United States Patent No. 1,543,569, and British Patents No. 230, 457 and No. 249,717. These products also give good dyeings on acetate silk when they contain only one sulfonic or carboxylic group, which must be present in the diazo component. Thus, the dye from 2,4-dinitro-aniline-6-sulfonic acid and omega-aminoethyl-*B*-naphthylamine on treatment with acetic anhydride at 65 to 75° C. (149 to 167° F.)

gives a product dyeing acetate silk a blue color and wool a greenish-blue color. 4-Nitroaniline-2-sulfonic acid and the monoacyl derivative of omega-aminoethyl-*B*-naphthylamine give a product dyeing acetate silk a reddish-violet and wool a violet color. 5-Nitro-2-aminobenzoic acid and omega-aminoethyl-*B*-naphthylamine give crystalline products dyeing acetate silk bluish-pink. Many other products are mentioned.

British Patent No. 257,654, May 29, 1925, to the British Dyestuffs Corporation, R. S. Horsfall, L. G. Lawrie, J. A. R. Henderson and J. Hill states that water soluble dyes which may be used for dyeing acetate silk, without the use of solubilizing or dispersing agents, are obtained from many acid and direct dyes by converting their sulfonic acid groups into sulfoamide groups by successive treatment with phosphorous pentachloride and ammonia. Or, alternatively, by the synthesis of dyes of the acid type from coupling components already containing the sulfonamide groups. In this manner a reddish-orange color is obtained by using the dyestuff prepared by combining diazobenzene with 1-naphthol-3, 8-disulfonamide (1 per cent), together with 1 to 2 per cent of formic or sulfuric acid at 74 to 77° C. (165 to 171° F.) for a half hour. Orange shades are obtained by using in a similar way the dyestuff prepared by coupling diazobenzene with 1,8-naphthasaltam. No dispersing agents are necessary in the application of these dyestuffs.

German Patent No. 420,017, June 12, 1923, to F. Gunther and F. Lange, assignors to the Badische Company, states that cellulose esters may be dyed with water soluble sulfamic acids of the dyestuff, and the colors obtained may be diazotized and developed with chromogens, or coupled with diazo compounds. Thus, the azo dye from *p*-aminophenylsulfamic acid and *B*-naphthol, used in acid solution, gives brownish-red shades, while further diazotization and treatment with *B*-naphthol produces a red-violet color.

German Patent No. 423,601, December 25, 1923, an addition to No. 418,490 (See British Patent No. 225,862), to the Bayer Company, assignees of W. Duisberg, W. Hentrich, and L. Zeh states that azo dyestuffs suitable for dyeing acetate silk are prepared by coupling diazotized amines or their substituted derivatives with

aralkylarylamines or their substituted derivatives containing carboxylic or sulfonic acid groups. For example, yellow, bordeaux, and orange-red dyes are obtained by coupling 5-nitro-2-anisidine and benzyl-*o*-sulfanilic acid, 2,4-dinitroaniline and 4-sulfobenzyl-2-toluidine, and 2,4-dinitroaniline and benzylanthranilic acid, respectively. Also see United States Patent No. 1,595,178.

United States Patent No. 1,574,748, March 2, 1926, to J. Baddiley and W. W. Tatum covers dyes of the general formula $A.NH.SO_2.(1)C_6H_3.COOH(3).OH(4)$, in which A represents an anthraquinone residue which may be substituted. As acid dyes they are directly applicable to wool, with or without a chrome mordant. They may also be applied to acetate silk. Among the starting materials used in their preparation are diaminoanthrarufin, or 1,4-diaminoanthraquinone, or 1,4,5,8-tetraaminoanthraquinone and salicylic sulfochloride. Very possibly these dyes are applied to acetate silk by the dispersol method. See British Patent No. 207,711.

United States Patent No. 1,575,324, March 2, 1926, to W. Duisberg W. Hentrich, covers acetate silk dyes of the type R.N :N.R′, in which R.N :N- stands for the diazo derivatives of an acid-substituted aromatic nitro compound and R for an aromatic diamine. For example, sodium 4-nitro-1-benzoate-2-azomethylbenzylaniline gives clear orange shades on acetate silk.

According to United States Patent No. 1,587,708, June 8, 1926, to W. Duisberg, W. Hentrich, C. Weinand, and L. Zeh, acetate silk and similar esters and ethers may be dyed with *o*-aminoanthraquinonesulfonic acid compounds, such as 1-aminoanthraquinone-2-sulfonic acid (orange), 2-aminoanthraquinone-1-sulfonic acid (yellow), 2-aminoanthraquinone-3-sulfonic acid (yellow), 1-amino-4-bromoanthraquinone-2-sulfonic acid (yellowish-red), 1-amino-5-toluinoanthraquinone-2-sulfonic acid (dark red), 1-amino-4-thiotolyanthraquinone-2-sulfonic acid (reddish-violet), and 1-amino-4-dihydroglyoxalylanthraquinone-2-sulfonic acid (violet).

United States Patent No. 1,595,178, August 10, 1926, to Duisberg, Hentrich and Zeh states that ammonium 2,6-dinitroaniline-4-sulfonate or other acid substituted dinitroanilines can be diazotized and the resulting diazo compounds coupled with *B*-naphthyl-

amine or other aromatic amines having no acid group in the molecule, to form dyestuffs suitable for dyeing acetate silk and the related esters and ethers. See German Patent No. 423,601.

In United States Patent No. 1,599,748, September 14, 1926, to Heinz Eichwede and Erich Fischer, assigned to the Grassilli Dyestuffs Corporation, it is stated that diethylanilinesulfonic acid and its substitution products, when coupled with unsulfonated aromatic diazo compounds of the benzene or naphthalene series containing at least one nitro group, yield dyestuffs which give deep shades of good fastness varying from yellow to violet on acetate silk and the related esters and ethers. For example: One kilogram of acetate silk is dyed a deep golden-yellow shade of good fastness by working for 45 to 60 minutes at 60 to 70° C. (140 to 158° F.) in a 20 or 25 liter dye bath containing 20 grams of the dyestuff prepared from diazotized 3-nitro-2-methyl-1-aminobenzene and diethylaniline-*m*-sulfonic acid, with or without the addition of a salt or an acid, or/and a protective colloid. If the 3-nitro-2-methyl-1-aminobenzene of the above example is replaced with 4-chloro-2-nitro-1-aminobenzene or 4-nitro-2-aminobenzene-1-carboxylic acid ester, or a similar base, deep orange shades of equally good fastness are obtained. The dyestuff obtained from 2,4-dinitro-1-aminobenzene and diethylaniline-*m*-sulfonic acid gives deep reddish-violet shades. This may cover some Cellit dyes.

In United States Patent No. 1,602,695, October 12, 1926, to R. Metzger, assigned to the I. G. Farbenindustrie Aktiengesellschaft, claim is made for the use of water-soluble sulfonic acids derived from colored amino compounds which are not dyestuffs in the usual sense, especially from aminoanthraquinones, as suitable for use in the dyeing and printing of the cellulose esters, including acetate silk. These sulfonic (sulfamic) acids may be used as such, or in the form of salts, and may contain one or several sulfamic ($NH—SO_3H$) residues with or without further substituents in their molecules. The dyeing process may be carried out in the usual manner, without any preliminary treatment of the acetate silk. In many cases the dyeings so obtained may be subjected to an after-treatment with diazo compounds or they may be diazotized and coupled with a suitable component, by which after-

treatments valuable new shades are obtained. Printing is carried out in the usual manner.

For example, the acetate silk may be entered into a luke-warm dye bath containing 3 per cent, on the weight of the goods, of the sulfonic acid sodium salt derived from 1,4-diaminoanthraquinone (30 per cent purity), 10 per cent of Glauber's salt, and 4 per cent of sulfuric acid. The temperature is slowly raised to 70 or 80° C. (158 or 176° F.) until a reddish-violet color is obtained. A somewhat lighter shade is obtained on substituting formic acid for the sulfuric acid. A redish-blue color is obtained in the same manner at about 75° C. (167° F.) with 3 per cent of the sodium salt of 1,5-disulfamic-acid-4, 8-dihydroxyanthraquinone (54 per cent purity), adding 10 per cent of sodium bisulfate in one or several portions.

The acetate silk may be printed in bright bluish-red colors with a paste containing 50 parts of the sulfamic acid sodium salt derived from 1-amino-4-methoxyanthraquinone (43 per cent purity) dissolved in 50 parts of glycerol and made into a paste with 900 parts of thickening. The printed material is dried, steamed, and rinsed.

### *The "Sulfato" Dyes—Their Preparation, Patents, and Application to Acetate Silk*

The application of an entirely new class of dyestuffs to acetate silk is covered by British Patent No. 237,739, August 22, 1924, to the British Dyestuffs Corporation, W. H. Perkin and S. C. Bate. This patent states that a few of the sulfato dyestuffs,[a] described in British Patent No. 181,750, may be applied to acetate silk from neutral, acid, or alkaline dye baths to give a variety of shades of good fastness to light and washing. The nitrated monoazo dyes of this class appear to give the brightest shades.

For example, acetate silk may be dyed a bright scarlet by immersion for an hour at 60 to 80° C. (140 to 176° F.) in a dye bath containing 3 per cent of salt, 1 per cent of sulfuric acid and 1 per cent of the dyestuff obtained by coupling diazotized *p*-nitroaniline with sodium sulfatoethylaniline. Sulfato dyestuffs con-

[a] A. G. Green and K. H. Saunders, *J. Soc. Dyers and Colourist 39,* 39-42 (1923).

taining amino groups, such as *p*-aminobenzeneazo-*p*-sulfatoethylaniline, may be used and the resulting shades subsequently diazotized and developed by the usual methods. Two-color effects on union materials containing cotton and acetate silk are obtained by dyeing in one bath with sulfato dyestuffs having an affinity for either, but not both of the fibers.

Sulfato compounds suitable for dyeing acetate silk are obtained by coupling *m*-nitroaniline with sulfatoethylaniline (reddish-yellow), or ethylsulfatoethylaniline (yellowish-orange); *p*-nitroaniline with sulfatoethylaniline (reddish-orange), or sufatoethyl-*o*-toluidine (bright red), or ethylsulfatoethylaniline (scarlet), or sulfatoethyl-*B*-naphthylamine (bright pink), or sulfatoethyl-*a* naphthylamine (magenta); 1-nitro-2-naphthylamine with methylsulfatoethylaniline (orange); 4-nitro-1-naphthylamine with ethylsulfatoethylaniline (brown); or 3,5-dinitro-*o*-toluidine with ethylsulfatoethylaniline (cardinal red). *o*-Chloro-*p*-nitroaniline with ethylsulfatoethylaniline (bluish-red), or sulfatoethyl-*a*-naphthylamine (bright violet); 2,4-dinitroaniline with benzylsulfatoethylaniline (bluish-red), or sulfatoethyl-*a*-naphthylamine (navy blue); and 2,4-dinitro-1-naphthylamine with sulfatoethyl-*a*-naphthylamine (greenish-blue).

The original patent covering these new "sulfato" dyes was British Patent No. 181,750 (1922), to the British Dyestuffs Corporation, A. G. Green and K. H. Saunders, and United States Patent No. 1,483,084, February 12, 1924, was based upon the discovery that the presence of the alcoholic sulfuric group, $—C_2H_4.SO_4H$, attached to nitrogen, has a somewhat similar function to the sulfonic acid group in dyes. The resulting dye is therefore soluble; acid in character, and therefore suitable for dyeing real silk and wool. Apart from the fact that these properties are characteristic of these new dyes, their use is not restricted to the dyeing of animal fibers, as it was originally recognized that some of them would dye cotton from a neutral or alkaline dye bath, while others may be used in the manufacture of lakes and pigments. Members of this group suitable for use as mordant dyes were also prepared. Now it has been discovered that certain dyes of this class are suitable for acetate silk, so that it may be

possible to dye almost any combination of fibers in certain colors with this one class of dyes.

One or more "sulfato" groups ($SO_4H$), like the sulfonic acid group, may be introduced not only into the finished dye, but also into one or both components used in the production of the dyestuff. The number of sulfato groups which may be introduced depends only upon the number of replaceable hydrogen atoms attached to nitrogen which are present. British Patent No. 186,878 covers the preparation of compounds suitable for sulfation.

There is also another quite distinctive method which involves the use of ethylene chlorhydrin. This is first allowed to react in aqueous or alcoholic solution with a primary or secondary amine or diamine of the aromatic or fatty-aromatic series, or one of their derivatives, so that an intermediate product containing the hydroxyethyl residue ($—C_2H_4.OH$) is formed. This product is then converted into a hydroxyethyl dyestuff, which, on subsequent treatment with concentrated sulfuric acid, yields the required soluble dyestuff containing the sulfato group attached to the ethyl residue. Thus, if R represents a chromophoric nucleus, the new dyestuffs would be represented by $R.NH.C_2H_4.SO_4H$ or $R.N(C_2H_4.SO_4H)_2$. For example, hydroxyethylaniline, $C_6H_5.NH.C_2H_4.OH$, obtained by the action of ethylene chlorydrin upon aniline is readily converted by sulfuric acid into phenylaminoethylhydrogen sulfate, $C_6H_5.NH.C_2H_4.SO_4H$, a colorless crystalline solid with acid properties which forms easily soluble salts.

Other chlorhydrins may be used in the same manner, and if desired, a sulfonic acid group may be introduced at the same time as the sulfato group, however this would possibly not be desirable in products for use in dyeing acetate silk. While the above mentions only the sulfatoethyl derivatives, other sulfato-alkyl compounds may be prepared and used in a similar manner. Thus, by reacting with glycerol mono-, di-, or epi-chlorhydrin upon an amino compound and treating the product with sulfuric acid, sulfatohydroxypropyl derivatives are obtained, containing for example the group $—NH.C_3H_5(OH).SO_4H$. These latter dyestuffs appear to be less brilliant than the sulfatoethyl derivatives. The principal may be applied to almost any class of dyestuffs containing

nitrogen, for the preparation of "acid" dyes. The various chlorhydrins may be used in the same manner.

A modification of the foregoing method consists of first forming *B*-chlorethylhydrogen sulfate by dissolving ethylene chlorhydrin in concentrated sulfuric acid,

$$C_2H_4Cl.OH + H_2SO_4 \longrightarrow C_2H_4Cl.SO_4H + H_2O,$$

and then allowing this compound to react in a neutral or alkaline solution with a dyestuff component, intermediate product, or a dyestuff containing a primary or secondary amino group. In this manner the sulfatoethyl group may be introduced by a single step; $R.NH_2 + C_2H_4Cl.SO_4H \longrightarrow R.NH.C_2H_4SO_4H + HCl$. When ethylenechlorhydrin is used in the preparation of the sulfato intermediate product, the general structure of the monoamino derivatives in either

$$\begin{matrix} R \\ A \end{matrix}\!\!>N—C_2H_4.SO_4H \text{ or } R—N\!\!<\!\!\begin{matrix} C_2H_4.SO_4H \\ C_2H_4.SO_4H, \end{matrix}$$

in which R indicates an aromatic, or substituted aromatic residue, and A represents a hydrogen atom or an alkyl, oxalkyl, aralkyl or aryl group. An aromatic diamine may be converted into a mono-, di-, tri-, or tetra-sulfato acid.

To convert the hydroxethyl intermediate compound into its sulfato acid, it is only necessary to use sulfuric acid, or a substitute, of the same concentration as is used in the preparation of ethylhydrogen sulfate, the general conditions being the same in both cases. The resulting product may be used for the direct preparation of a sulfato dye.

Parent basic dyestuffs are prepared from their hydroxyethyl components in a manner similar to that used for the corresponding dyes from ethyl- and diethylanilines, ethyl-*o*-toluidine, ethyl-*a*- and *B*-naphthylamines, dialkyl-*m*-phenylenediamines, etc. They are then treated with sulfuric acid. Both of the foregoing methods are applicable to all classes of dyes in which the members can be obtained as the corresponding ethyl derivatives.

In the same manner, sulfato triphenylmethane dyes can be obtained by condensing a sulfato intermediate with suitable aldehydes, while all types of dyes obtainable from nitroso compounds by condensation with amines, phenols, or aminophenols, can be prepared from nitroso sulfato acids, or a hydroxyethylazine, oxazine,

or thiazine dye may be converted into its sulfato acid. It is possible that prior to this invention sulfato compounds have been prepared but not recognized.

As an example of the preparation of these dyes, the sodium salt of *p*-nitrobenzeneazo-*p*-disulfatodiethylaminobenzene is prepared by adding to a solution of 23.1 parts of the sodium salt of disulfatodiethylaniline, a solution containing 10 parts of diazotized *p*-nitroaniline. Coupling takes place in the presence of acetic acid and the dye is salted out. It is a red powder which dyes wool scarlet from an acid dye bath and has the formula

$$C_6H_4(NO_2).N_2.C_6H_4.N(C_2H_4.SO_4Na)_2.$$

The same dyestuff may be prepared in another manner by dissolving 12.3 parts of dihydroxyethylaniline in dilute acid and coupling it with the diazo solution prepared from 10 parts of *p*-nitroaniline. The insoluble red powder is dried, and 1 part is heated with 2 or 3 parts of concentrated sulfuric acid at about 30 to 100° C. until it is soluble in dilute alkali. The melt is then diluted and the dye salted out as before.

The sodium salt of disulfatodiethylditolyphenylcarbinol may be prepared by slowly adding 10 parts of the dyestuff obtained according to British Patent No. 13,604 (1914) (by condensing benzaldehyde with oxethyl-*o*-toluidine and subsequent oxidation with lead oxide) to 20 or 30 parts of cold concentrated sulfuric acid, keeping the temperature down. The solution is allowed to stand until the product is soluble in alkali. On dilution and salting out, a dyestuff is obtained which dyes wool greenish-blue from an acid dye bath. The leuco base may be sulfonated before oxidation to the carbinol. This dye has the formula

$$C_6H_5.C(OH)\Big<\begin{matrix}C_6H_3(CH_3).NH.C_2H_4.SO_4Na.\\ C_6H_3(CH_3).NH.C_2H_4.SO_4Na.\end{matrix}$$

Sulfatoethylaminodioxytoluphenoxazoniumcarboxylic acid,

$$(C_2H_4SO_4Na)\,.\,NH\,.\,C_6H_2(CH_3\Big<\begin{matrix}N\\ O\end{matrix}\Big>\underline{C_6H(OH)_2\ \ CO}_2,$$

may be prepared from a dyestuff of the gallocyanine type. This gallocyanine dye is prepared by the usual method from *p*-nitrosooxyethyl-*o*-toluidine and gallic acid.[b] Ten parts of this dye are

[b]See British Patent No. 182,031 of 1921.

added to 20 or 30 parts of concentrated sulfuric acid and the solution warmed until it gives no precipitate in a tannin reagent. It is then diluted and the dyestuff salted out as a black powder which dyes wool a deep blue from an acid dye bath and chrome mordanted wool a violet blue.

All types of dyestuffs do not yield sulfato compounds with equal ease and it has been observed that the finished dyestuff of the triarylmethane and quinonimide types, that is compounds having the quinonoid structure, are particularly easy to sulfate, so that even cold sulfuric acid may be used. Under such conditions it is found that solubility in alkali is attained in a few minutes, and upon pouring the sulfuric acid solution onto ice, and adding salt, the sulfato dyestuff separates and may be collected. On the other hand, many leuco bases require to be heated with the acid at 100° C. for some time to complete the sulfation. The advantages of sulfation over sulfonation is particularly apparent with the triarylmethane and quinonimide type of dyes which are not easily built up from sulfonated intermediates and which are readily spoiled by sulfonation with oleum. Sulfation allows any given hydroxyalkyl dyestuff with basic properties to be converted into an acid dyestuff, while the mild treatment necessary does not dull the shade.

The sulfato dyes have all of the usual characteristics of the acid dyes and little difference will be noticed in their application and that of the nearest related sulfonated dyestuff. As a class, the sulfato dyes are more level-dyeing than the sulfonated products, and the exhaustion of the dye bath is about the same. No hydrolysis appears to occur in the dye bath and the fastness of the resulting colors appears to be about the same as that obtained from the corresponding sulfonated dye.

Probably some of these sulfato dyes may find use upon fiber combinations containing acetate silk and wool or true silk. As they are applied to animal fibers by the usual acid dyeing methods, in certain instances the acetate silk may also be dyed a somewhat similar shade, the comparison with the shade of the wool depending upon the particular dye used and the conditions of application. Also see the omega-sulfonic dyes discussed as Ionamines.

# CHAPTER XV

# THE DIRECT COTTON, SULFUR, AND VAT DYES ON ACETATE SILK

*Their Preparation, Application and Patents*

IT is a well-known fact that fully sixty per cent of the direct cotton dyes have no affinity for acetate silk. However, as mentioned in Chapter XIII, when applied to acetate silk, the members of the acid and mordant classification are applied by the "direct" method. While the true dispersol products are usually an entirely different type of product from any of those mentioned above, when they are considered according to their method of application, they too, come under the direct class. However, under the above subtitle, we will only consider the dyes of the older classification known as the Direct Cotton dyes. Very few of these dyes are applicable to acetate silk except by special methods, such as saponification, which will be considered later. The Setacyl Direct dyes of Geigy and the Cellit dyes of Bayer could be classed as Acetate Silk Direct dyes, but they were considered under the acid dyes.

Among the few direct cotton dyes which are applicable to acetate silk should be mentioned Pyramidol Brown BG (C. I. No. 380, the sodium salt of diphenyldisazobisresorcinol), Paramine Orange G, Paramine Orange R (C. I. No. 415, the sodium salt of diphenyldisazosalicylic-acid-*a*-naphthylamine-4-sulfonic acid), Paramine Yellow 2G (C. I. No. 43, the sodium salt of *p*-nitrobenzenedisazoaminosulfobenzenylaminothiocresol), and Paramine Brown G (C. I. No. 596, the sodium salt of *p*-sulfobenzeneazo-*m*-phenylenediamineazodiphenylazosalicylic acid). Chlorazol Black E extra (C. I. No. 581, the sodium salt of benzeneazo-3,6-disulfo-8-amino-1-naphthol-7-azodiphenylazo-*m*-phenylenediamine) stains Celanese a deep red-gold, undoubtedly due to a basic impurity. These dyes may be applied by Method No. 53.

*Method No. 53: Direct Cotton Dyes on Acetate Silk.* Start cold

and raise the temperature at 76° C. (170° F.) in about one-half hour. Dye at this temperature for a half-hour and cool one-half hour, using 10 to 30 per cent of salt in the dye bath.

There is a wide variety of direct dyes which do not stain acetate silk and a list of these dyes will be found under the dyeing of acetate silk-cotton unions, Chapter XXXIII. In selecting direct dyes for use upon such unions, where the acetate silk should not be stained, care must be taken to obtain direct cotton dyes which do not contain either basic impurities or shading components of basic dyes. If this precaution is not taken, various lots of the same direct cotton dyestuff may stain the acetate silk in different and entirely unexpected shades, much to the consternation of the dyer. United States Patent No. 1,398,357 and British Patent No. 158,340 cover a process of increasing the affinity of acetate silk for various dyes, including the direct cotton dyes, by means of ammonium thiocyanate.

### *The Sulfur Dyes on Acetate Silk*

A few sulfur dyes are probably applicable to acetate silk if applied in a hydrosulfite vat in the same manner as the ordinary vat dyes to cotton, but giving particular attention to the alkalinity and temperature of the dye bath, so as to avoid saponification of the acetate silk. They are of course also applicable by the saponification process, which will be discussed later in Chapter XIX and are used to some extent upon the cotton of acetate silk-cotton unions, but by special methods. British Patent No. 179,384, Chapter XI, covers their application by precipitation. The sulfur dyes may also be printed upon acetate silk in an alkaline paste, as will be mentioned under printing, Chapter XXIV.

Clavel obtained British Patent No. 191,553, Nov. 19, 1921, on a process for applying full shades to acetate silk with either sulfur or vat dyes. According to this patent, the dye should be reduced by hydrosulfite in a bath feebly alkaline by ammonia and containing only sufficient caustic alkali to combine with the leucobase of the dyestuff, but not enough to hydrolyze the acetate silk. Exhaustion of the dye bath is effected by the addition of salts, such as the chlorides of calcium, barium, and magnesium, precipita-

tion being prevented by the addition of protective colloids, such as gelatin, silk boil-off liquor, glucose, starch, etc.

### *Vat Dyes on Acetate Silk*

As the vat dyes are usually applied to all fibers from a more or less strongly alkaline dye bath or "vat," they are not particularly suited for application to acetate silk; however, certain of the Indigoid vats may be applied to acetate silk with more or less success under suitably modified conditions. Since the discovery of the dispersol dyes, there is really no reason to apply them to acetate silk as many of the products applied by the dispersol method have all the good properties of the vat dyes on acetate silk, are easier to apply with less chance of injuring the fiber, and give more brilliant shades.

On account of its greater resistance to alkalies and high temperatures, Lustron is possibly better suited to receive these products than some other varieties of this fiber. The "Ciba" vat dyes of the Ciba Company have been applied to Celanese, and probably certain Helindone, Brilliant Indigo, Thioindigo and Durindone brands may also be applied.

The fact that vat dyes, by the alkaline hydrosulfite vat method, do not follow the same general fastness laws on acetate silk as on cotton, and that the later dyes (dispersol) developed especially for acetate silk have an even greater fastness upon it than the vat dyes, reduces their importance for this fiber very materially. As a class the vat dyes on acetate silk all show a tendency to rub off badly and their application requires a very careful adjustment of alkalinity and hydrosulfite, in order to avoid hydrolysis of the fiber.

Certain vat dyes, as for instance Indanthrene Bordeaux B, Algol Rose R, Algol Scarlet G, Algol Yellow WG, Algol Violet B, as well as some of the Anthrene dyes, are absorbed by acetate silk from aqueous suspensions, as in the dispersol process, and the resulting colors have an excellent fastness. With the present wide use of the anthraquinone derivatives by this newer method of application, there is possibly not much use for the application of the vat dyes to acetate silk by means of the alkaline hydrosulfite vat, except in very special cases, such as upon acetate silk-cotton unions. The anthraquinone dyes, when applied by the

dispersol methods, appear to have all of the fastness properties looked for in the vat dyes, and even greater fastness to crocking than when applied to acetate silk by the usual vat methods. Deeper shades are also usually obtainable by the dispersol methods. Certain vat dyes are also applicable to acetate silk by precipitation methods, as mentioned under British Patent No. 179,384.

The Lustron Company states that some vat dyes may be applied to Lustron, but that the Indanthrene vats usually give only pale shades. The alkalinity of the bath should of course be kept as low as possible, and by gradually raising the temperature to a moderate degree, full vat shades can be put on Lustron with some vat dyes. Level shades are only obtained by working the goods well while dyeing. This treatment somewhat impairs the water resistance of Lustron, possibly owing to a partial saponification, but they state that it will be twice as strong as the other rayons when wet.

Briggs[1] states that vat dyes, including the Indigoid and those of the Algol and Indanthrene class which can be used without caustic soda, are suitable for use in dyeing unsaponified acetate silk. Saponification during dyeing is inhibited by the presence of an ammonium salt. One of the earliest successful methods of applying the vat dyes to acetate silk was developed by the Ciba Company for their "Ciba" dyes. Their color card showing these dyes on Celanese gives many desirable shades. Method No. 54 gives their formula for application.

*Method No. 54: Ciba Vat Dyes on Acetate Silk.* The "stock vat" is prepared by working one pound of the vat dye in powder form, or an equivalent amount of paste, into a smooth paste with 1.5 pints of 66° Tw. (1.330 sp. gr.) sodium hydroxide solution and 3 ounces of Monopole soap. When the dyestuff is used in paste form, except in the case of Ciba Orange G paste, the addition of Monopole soap can be omitted. This paste is mixed with 20 gallons of hot water and while stirring well, one pound and three ounces of hydrosulfite concentrated is added gradually, and the whole allowed to stand for about a half hour. Table XXIX gives the equivalent weight of the dyes in powder and paste forms, the proper temperature of the stock vat and the color of the vat when properly reduced.

TABLE XXIX
TEMPERATURE OF THE STOCK VAT AND CONCENTRATION OF DYESTUFFS IN PASTE AND POWDER FORMS

| *Name of Dye* | *Paste* | *Parts of Powder* | *Temperature of Stock Vat °F.* | *Color of Reduced Vat* |
|---|---|---|---|---|
| Ciba Yellow G | 100 | 10 | 140 | Dull reddish-violet |
| Ciba Orange G | 100 | 13.5 | 122 to 140 | Dull brownish-olive |
| Ciba Brown R | 100 | 12.5 | 140 | Brownish-yellow |
| Ciba Scarlet G extra | 100 | 20 | 104 | Bluish-violet |
| Ciba Red R | 100 | 10 | 104 | Bluish-violet |
| Ciba Red G | 100 | 10 | 158 | Reddish-yellow |
| Ciba Pink G | 100 | 10 | 104 to 122 | Dull yellowish-brown |
| Ciba Pink B | 100 | 20 | 140 | Reddish-yellow |
| Ciba Pink BG | 100 | 10 | 140 | Greenish-yellow |
| Ciba Violet B | 100 | 10 | 158 | Dull golden yellow |
| Ciba Violet 3B | 100 | 10 | 158 | Golden yellow |
| Ciba Blue 2B | 100 | 16 | 158 | Golden yellow |
| Ciba Blue 2G | 100 | 16 | 158 | Yellowish-olive |
| Ciba Green G | 100 | 10 | 158 | Reddish-orange |
| Indigo Ciba R | 100 | 20 | 122 | Golden yellow |

The "dye vat" is prepared by adding three ounces of 30 per cent ammonia, one ounce of hydrosulfite concentrated powder, and six ounces of fish glue, previously dissolved in water, to each 200 gallons of bath at 71° C. (160° F.). The dye solution from the "stock vat" is then added to the dye vat through a fine sieve or cloth.

The scoured goods, if dry, are wet-out in a bath containing 25 ounces of olive oil soap and 25 ounces of ammonia, per hundred gallons of liquor, at 55 to 60° C. (130 to 140° F.) for one-half hour and are then entered into the completed dye vat and dyed at 65-71° C. (150-160° F.) for an hour, with the addition of 2 to 5 ounces of salt per gallon of liquor. After dyeing, the material is hydroextracted and allowed to oxidize in the air for 2 to 3 hours. It is then rinsed and soaped in a bath containing 50 ounces of olive oil soap per hundred gallons at 71° C. (160° F.) for one-half hour. With Ciba Violet or mixtures containing it, after oxidation in the air, the goods should receive an additional treatment for a half hour at 71° C. in a bath containing 2 per cent of 40 per cent acetic acid, on the weight of the goods. It is then rinsed again and soaped as above. The formulas in Table XXX will give an idea as to the dyes and amounts used to obtain the various shades on Celanese.

TABLE XXX

Colors on Celanese with Ciba Dyes

| | | |
|---|---|---|
| Bambino | 0.07% | Ciba Blue 2G powder |
| Cherub | 0.2% | Ciba Scarlet G extra powder and |
| | 0.8% | Ciba Yellow G paste |
| Gray | 0.23% | Ciba Blue 2B powder |
| | 1.5% | Ciba Orange G paste and |
| | 0.04% | Ciba Red G powder |
| Hollyhock | 3.2% | Ciba Pink B powder and |
| | 0.25% | Ciba Violet B powder |
| Canary | 3.0% | Ciba Yellow G paste |
| Pangoon | 48.0% | Ciba Orange G paste |
| | 1.0% | Ciba Red G powder and |
| | 2.0% | Ciba Indigo R paste, 20% |
| Pink | 0.7% | Ciba Pink G powder |
| Pigeon | 1.2% | Ciba Blue 2B powder |
| | 6.0% | Ciba Orange G paste, and |
| | 0.5% | Ciba Red G powder |
| Bonfire | 8.0% | Ciba Red G powder |
| Taffy | 3.0% | Ciba Orange G paste |
| | 0.03% | Ciba Red G powder and |
| | 0.02% | Ciba Blue 2B powder |
| Celestial | 0.5% | Ciba Blue 2G powder |
| Putty | 0.25% | Ciba Blue 2B powder |
| | 4.5% | Ciba Orange G paste and |
| | 0.13% | Ciba Red G powder |
| Tangerine | 32.0% | Ciba Orange G paste and |
| | 8.0% | Ciba Pink BG paste |
| Mignonette | 0.45% | Ciba Blue 2B powder |
| | 4.0% | Ciba Orange G paste and |
| | 0.03% | Ciba Red G powder |
| Taupe | 0.6% | Ciba Blue 2B powder |
| | 4.5% | Ciba Orange G paste and |
| | 0.25% | Ciba Red G powder |
| Brickdust | 8.0% | Ciba Brown R paste |
| | 2.0% | Ciba Red G powder and |
| | 16.0% | Ciba Orange G paste |
| Amethyst | 0.9% | Ciba Violet 3B powder and |
| | 0.1% | Ciba Blue 2B powder |
| Congo | 5.5% | Ciba Indigo R paste 20% |
| | 32.0% | Ciba Orange G paste and |
| | 1.2% | Ciba Red G powder |
| Maple sugar | 0.12% | Ciba Blue 2B powder |
| | 2.5% | Ciba Orange G paste |
| | 0.1% | Ciba Red G powder |
| Cream | 0.2% | Ciba Orange G paste and |
| | 0.15% | Ciba Yellow G paste |
| Spice | 30.0% | Ciba Orange G paste |
| | 10.0% | Ciba Brown R paste and |
| | 5.0% | Ciba Yellow G paste |
| Electric | 1.2% | Ciba Blue 2B powder |
| | 1.6% | Ciba Orange G paste and |
| | 1.6% | Ciba Yellow G paste |

TABLE XXX

Colors on Celanese with Ciba Dyes

| | | |
|---|---|---|
| Pearl | 0.20% | Ciba Blue 2B powder |
| | 1.30% | Ciba Orange G paste and |
| | 0.08% | Ciba Red G powder |
| Meadowlark | 0.7% | Ciba Blue 2B powder |
| | 9.0% | Ciba Orange G paste and |
| | 0.3% | Ciba Red G powder |
| Golden Glow | 12.0% | Ciba Yellow G paste and |
| | 8.0% | Ciba Orange G paste |
| Apple Blossom | 1.0% | Ciba Red G powder |
| | 0.12% | Ciba Violet B powder and |
| | 0.6% | Ciba Orange G paste |
| Fudge | 2.8% | Ciba Indigo R paste 20% |
| | 35.0% | Ciba Orange G paste, and |
| | 1.2% | Ciba Red G powder |
| Vervain | 0.14% | Ciba Violet 3B powder |
| Asphalt | 0.65% | Ciba Blue 2B powder |
| | 7.5% | Ciba Orange G paste and |
| | 0.16% | Ciba Red G powder |
| Champagne | 0.9% | Ciba Orange G paste and |
| | 0.01% | Ciba Red G powder |
| Lead | 0.9% | Ciba Blue 2B powder |
| | 5.0% | Ciba Orange G paste and |
| | 0.22% | Ciba Red G powder |
| Columbia | 2.0% | Ciba Blue 2G powder |
| Chutney | 2.5% | Ciba Indigo R paste 20% |
| | 36.0% | Ciba Orange G paste and |
| | 2.0% | Ciba Red G powder |
| Lotus | 0.5% | Ciba Red G powder |
| | 0.2% | Ciba Pink BG powder |
| Chinese Green | 38.0% | Ciba Green G paste and |
| | 10.0% | Ciba Yellow G paste |
| Banner | 8.0% | Ciba Blue 2B powder |

No doubt many of the Helindone vat dyes can be applied by Method No. 54, only using formulas along the line of those usually given for Helindone dyes on wool.[2] Durindone Red Y, Ciba Blue and Indigo Blue paste have also been mentioned in the literature as applicable to acetate silk. Perhaps Method No. 101 (sodium phenolate) may also be useful in applying certain vat dyes to acetate silk.

Most of the Indanthrene vat dyes of the older classifications do not appear to be particularly applicable to acetate silk by the regular hydrosulfite vat methods on account of the high alkalinity of the dye bath required to hold them in solution. However, some of them, as well as certain Caledon vats, have some application to

the cotton of acetate silk-cotton unions, but extreme care must be exercised to avoid saponification of even the Lustron variety of acetate silk. Many of them may be applied to the acetate silk by the saponification process which will be discussed later.

*Method No. 55: Indigo on Acetate Silk.* Indigo may be applied to acetate silk superficially from a fine suspension in water as in the dispersol process, or the fiber may be dyed to deep blue shades from the regular leuco-indigo vat containing glue and a small quantity of hydrosulfite and ammonia, similar to Method No. 54. Indigosol, the new soluble form of indigo, does not appear to have quite as much affinity for acetate silk as leuco-indigo applied by the above method. The same may be said of the Soledon dyes, while the same vat dyes, by the dispersol process, sometimes have considerable affinity for acetate silk.

The Indophenols are more or less obsolete as dyes on the older fibers but according to Lawrie,[3] they may be useful on acetate silk. These dyes belong to the naphthoquinonemonoimide series. Lawrie states that Indophenol may be applied to acetate silk according to Method No. 56.

*Method No. 56: Indophenol on Acetate Silk.* Prepare the dye vat with 10 parts of Indophenol to each part of 76° Tw. (1.38 sp. gr.) sodium hydroxide solution, and 7.5 parts of hydrosulfite powder. This gives a good deep blue but the color is very sensitive to alkalies. It is possible that the use of an ammonia salt, such as the acetate, chloride, or sulfate, may have some protective action on the acetate silk from the alkali. Also a colloid such as glue might assist this protective action.

British Patent No. 214,112, May 20, 1923, to W. Kilby and Morton Sundour Fabrics states that acetate silk may be dyed by means of the alkaline (sodium hydroxide) hydrosulfite vat with amino- or nitro- derivatives of anthraquinone or their alkyl or halogen derivatives. The derivatives containing hydroxy groups have a decreased affinity for this fiber. Compounds such as $a$-aminoanthraquinone (yellowish-orange); $B$-aminoanthraquinone (lemon yellow); 1, 5-dinitroanthraquinone (yellowish-orange); 1, 5-diaminoanthraquinone (orange); 1, 4-diaminoanthraquinone (reddish-violet); 1-methylaminoanthraquinone (pinkish-red); 1-

amino-2, 4-dibromoanthraquinone (yellowish-orange); 1-nitro-4-chloroanthraquinone; 1-methyl-2-aminoanthraquinone, and 1-amino-5-chloroanthraquinone, are applicable by this method. In suitable instances the dye may be diazotized on the fiber and coupled with developers such as *B*-naphthol, whereby different shades are obtained.

According to British Patent No. 220,505, March 17, 1923, to the British Celanese Company, and United States Patent No. 1,545,819, July 14, 1925, to G. H. Ellis but assigned to the American Cellulose and Chemical Company, which appears to cover the same process, certain dyestuffs of the aryl- or substituted aryl-benzo- or naphthoquinonemonoimide series (Indophenols) have a very good direct affinity for acetate silk, giving blue and violet shades not directly obtainable with azo dyes. It had formerly been proposed, in British Patent No. 219,349 which will be discussed with the dispersol patents, to apply the Indophenols by the dispersol process. The present method covers their application from the usual alkaline hydrosulfite vat. These leuco-compounds are readily absorbed by the acetate silk fibers and upon oxidation, either in the air or by means of hypochlorites, peroxides, or other oxidizing agents, colors are obtained which are usually fast to soaping and light.

For example, a deep royal blue may be obtained on 100 kilograms of acetate silk by dissolving a kilogram of dimethyl-*p*-aminophenyl-1,4-naphthoquinonemonoimide and an equal weight of sodium hydroxide in a hundred liters of water. This is reduced with 2 kilograms of sodium hydrosulfite, and when reduction is complete, filtered into the 30 to 1 dye bath at 50° C. (122° F.), already containing 0.5 gram of sodium hydrosulfite and 2 cubic centimeters of concentrated ammonia, per liter. The material is worked for about an hour and a half, adding alkali or hydrosulfite as required to hold the dye in solution, after which the material is rinsed in cold water and finally oxidized in a bath containing 2 grams per liter of sodium perborate at 40° C. (104° F.) for 30 minutes.

British Patent No. 233,813, February 27 and November 22, 1924, to the British Dyestuffs Corporation, J. Baddiley and H.

Browning, Jr., states that acetate silk may be dyed by means of aqueous suspensions (dispersol method) of vat dyes of the indigo class, as well as certain indophenol dyes in the reduced or unreduced form. (See British Patents No. 219,349 and No. 220,505.) This patent covers the use of quinoneanilides and their substitution products and homologues, such as the thiazines, azines, or oxazines, in the ordinary hydrosulfite vat at 20° C. (68° F.), with a minimum of alkali so that the acetate silk is not appreciably hydrolyzed. Deep shades are readily obtained. For example: The condensation product of benzoquinone and *p*-chloraniline dyes acetate silk a brownish-yellow shade; that from *a*-naphthaquinone and diphenylamine gives a violet shade; while the product obtained by treating the base derived from *B*-naphthaquinone-4-sulfonic acid and *p*-toluidine with sulfur dichloride, gives red shades. Many other examples are also given.

In United States Patent No. 1,546,969, July 21, 1925, R. Clavel covers the same process as British Patent No. 191,553, given under the sulfur dyes and protects a process for dyeing acetate silk with vat dyes, such as bromoindigo or pyrogene indigo, by means of a hydrosulfite vat kept weakly alkaline with ammonia, caustic alkali only being added in sufficient quantity to form the leuco compound of the dye. The dye vat should also contain a protective colloid such as gelatin, glucose or starch, and at least one water soluble salt, as for instance the chloride of calcium, magnesium, or barium.

United States Patent No. 1,532,427, given under the dyeing "assistants," Chapter X, covers the application of certain vat dyes, such as Indanthrene Blue GCD paste (C. I. No. 1113) with sodium dicresyl phosphate, protective colloids, alkali and hydrosulfite. United States Patent No. 1,398,357 and British Patent No. 158,340, Chapter X, cover a method of increasing the affinity of the vat dyes for acetate silk by means of ammonium thiocyanate.

### *References*

[1] J. F. Briggs, *J. Soc. Dyers and Colourists 37,* 287-96 (1921).
[2] C. E. Mullin, *American Dyestuff Reporter 13,* 809-15 (1924).
[3] L. G. Lawrie, *J. Soc. Dyers and Colourists 40,* 69-74 (1924) and *American Dyestuff Reporter 13,* 593 (1924).

# CHAPTER XVI

# THE DEVELOPED OR AZOIC COLORS ON ACETATE SILK

*The Theory, Patents, and Components Used, As Well As The Methods of Application. The Oxidized Blacks*

ACETATE silk has a decided affinity for the organic bases, such as *p*-nitroaniline, *m*-nitro-*p*-toluidine, dianisidine, *a*-naphthylamine, benzidine, etc., and these bases may then be diazotized and developed on the fiber, with suitable naphthols or phenols, to give a wide variety of colors. As most of these bases are comparatively insoluble in water, they are usually converted into their hydrochlorides, which are water soluble, before being placed in the dye bath. They are then applied either as the hydrochloride, or by what is generally a more satisfactory process, the hydrochloric acid present may be neutralized in the bath, by the addition of alkali, thus precipitating the free base in the dye bath as a fine suspension. These free bases, in the form of a very fine aqueous suspension, have a much greater affinity for the acetate silk fiber than their hydrochlorides. For this reason the two different methods of application frequently give quite different shades on the fiber. Pokorny[7] obtained excellent results on a laboratory scale by dissolving the insoluble intermediate (base) in alcohol and pouring this into cold water; or by adding alcohol to the aqueous solution of the water soluble intermediate, in order to produce a fine suspension.

Many nitrogen compounds have a decided affinity for acetate silk and this is particularly the case with the amino compounds. In fact Greenhalgh[1] points out that acetate silk has a greater affinity for this group than almost any other group found in dyestuffs and says that in some cases under certain conditions, it is difficult to completely diazotize the amino group of compounds on the acetate silk fiber, which he attributes to its high affinity for the cellulose ester.

In applying the developed colors to acetate silk it is advisable to use just the reverse of the usual method of applying them to cotton. In other words, instead of padding the fiber with the naphthol and then developing the color in a bath containing the diazotized base or amine, as on cotton, the acetate silk should first be treated with base or amine, and this diazotized on the fiber, either in the presence of the developing component, or before entering the developing bath. This is on account of the much greater affinity of the bases for this fiber, than that of the naphthols or phenols. If the process as used on cotton is attempted upon acetate silk, the shades are usually dull, the fastness poor, and the results generally unsatisfactory.

Still another method of applying the free bases to acetate silk depends upon the solubility of a number of them in certain dispersing agents, such as those used in the dispersol method of dyeing. The free base is in this way precipitated as a colloid in the dye bath and applied in about the same manner as when it is precipitated from its hydrochloride. The affinity of these free bases for acetate silk is quite considerable, and sufficient, in a number of instances, such as benzidine, toluidine, *p*-*p*'-diaminodiphenylamine, etc., to produce a black color on the fiber, even when applied from a cold solution. For more details regarding suitable dispersing agents and the application of the bases by the dispersol process, see the dispersol method of dyeing, Chapters XXI, XXII, and XXIII.

Theoretically, the application of the developed colors to acetate silk is very simple, but in actual practice it is not always so easy. Frequently it is very difficult to obtain level shades. Compound, light, and delicate shades or tints are also usually difficult, but heavier shades are easier. Most of the first special dyes for acetate silk consisted entirely of these bases and a very large number of them are still offered upon the market. At the present time their main use is for blacks and other fast heavy shades in connection with the developed dyes on cotton unions, such as hoisery, etc., as no really satisfactory direct dyeing blacks have as yet appeared upon the market for acetate silk. Dort[2] mentions their use on Celanese for special fast shades of light navy, red, and orange.

Among the special dyes for acetate silk which consisted either entirely or principally of these bases are the Acedronoles of Badische, the Acetylines of St. Denis, the Azoniles of M. L. B., the Azonines of Cassella, the Azoics of Griesheim Elektron, the Azoles of A. G. F. A., certain Ionamines of the British Dyestuffs Corporation, the Silkons of Griesheim Elektron, the S. R. A. Diazo Solamines and S. R. A. Blacks of the British Celanese Company, etc. Quite a few of these bases give a direct color on acetate silk, without development, but most of these are only light shades, while others are practically colorless until developed. Those giving light shades directly usually give a considerably darker shade upon development, which is generally much faster to washing than the direct shade.

The affinity of basic compounds containing diazotizable amino groups for acetate silk has resulted in their application by almost every method evolved for dyeing this fiber. In the early Ionamines, some of which are still in use, they were solubilized by means of omega sulfonic acid groups. We have already discussed their application by dispersol methods. All through the patent literature covering dyes for acetate silk, mention is made that certain of the products may be diazotized and developed upon the fiber.

In applying the developed colors on acetate silk, as, for instance, black by means of aminoazodimethylaniline, Ionamine A, or S. R. A. Black IV, both of which will be discussed in connection with the other dyes of these brands, it is best to diazotize and couple in the presence of as little light as possible. This point is particularly important on acetate silk as the nitrogen containing groups in some cases appear to act a little differently than on other fibers, probably due to an affinity for the acetate silk, with the result that sometimes, in the presence of light, the resulting diazo color is off shade, and "should be" blacks are brownish.

As examples of the use of the bases upon acetate silk, the following may be of interest. The fiber may be soaked for some time in a two per cent aqueous solution of aniline, diazotized in an acidified nitrite solution, and developed with a two per cent solution of sodium naphtholate, thus producing Sudan I on the fiber. Or the impregnated fiber may be treated with a warm acidulated

dichromate solution, as described under the oxidized blacks, to produce Aniline Black on the fiber. *p*-Nitroaniline Red (Para Red) can be produced on the fiber by first impregnating it with a *p*-nitroaniline solution, rinsing, diazotizing and developing with *B*-naphthol. Primuline may also be diazotized and developed on acetate silk to give a wide variety of shades.

When applied in this manner, aminoazobenzene gives an excellent yellow which upon diazotization and development with *m*-phenylenediamine becomes brown, with *m*-toluylenediamine a redder shade, with *B*-naphthol a scarlet, or with resorcinol an orange shade. Benzidine gives a rich brown when diazotized and developed on the fiber with *m*-phenylenediamine. *o*-Anisidine and chloranisidine may be coupled with *a* or *B*-naphthol, *m*-phenylenediamine or resorcinol to give good shades. Dichlorobenzidine coupled with *B*-naphthol gives a fine crimson, with *m*-phenylenediamine a browner shade, or with chloranisidine a rich orange. Dianisidine coupled with *B*-naphthol gives a fine purple; or with *a*-naphthylamine hydrochloride a rich brownish-red. *p*-Aminodiphenylamine, when oxidized on the fiber gives a splendid black, Diphenyl Black, as described under the oxidized blacks. Table XXXI gives a list of developed colors on acetate silk. The use of sodium acetate to increase the absorption of the bases from the dye bath has been suggested.

Pokorny[7] obtained Para Red on acetate silk by impregnating the fiber with a fine suspension of *B*-naphthol, prepared by pouring an alcoholic solution of the naphthol into water, washing to remove the adhering intermediate and treating the fiber with diazotized *p*-nitroaniline solution. He also used the reverse process in which the fiber was first treated with the diazotized *p*-nitroaniline and then with the *B*-naphthol suspension.

Pokorny[7] also used a two bath method, similar to British Patent No. 199,754, for the production of Para Red, wherein he dissolved equimolecular portions of *p*-nitroaniline and *B*-naphthol in separate portions of hot alcohol and then poured both of these solutions into the one bath. After the goods are worked for a few minutes in the fine suspension, they are washed and treated in a second bath containing equimolecular portions of sodium nitrite and hy-

drochloric acid. While the acetate silk is dyed red in this acid bath, cotton remains white.

TABLE XXXI

SOME DIRECT AND DEVELOPED COLORS ON ACETATE SILK

| *Constitution* | *Direct* | *Developed with* *B-Naphthol* | *B-Hydroxy-naphthoic acid* | *B-Aminodiphenylamine* |
|---|---|---|---|---|
| *m*-Aminobenzoic acid +*o*-anisidine | Yellow | Scarlet | Magenta | Gold |
| *m*-Aminobenzoic acid + anthranilic acid | Yellow | Red | Bluish-red | Olive |
| *p*-Aminosalicylc acid + *a*-naphthamine | Yellow | Violet | Reddish-blue | Olive |
| 5-Acetylamino-2-amino-4-methoxtoluene +*B*-hydroxynaphthoic acid (hydrolyzed) | Blue-violet | Greenish-blue | Blue | Reddish-violet |
| *m*-Aminobenzoic acid +*p*-xylidene + *m*-phenylenadiamine | Red | Reddish-brown | Reddish-brown | Brown |
| *m*-Aminobenzoic acid +*p* -xylidene + *a*-naphthylamine | Brownish-red | Reddish-violet | Reddish-blue | Brown |
| *m* Aminobenzoic acid +*m*-toluidene | Yellow | Scarlet | Bluish-red | ——— |
| Anthranilic acid + *o*-anisidine | Orange | Bluish-red | Reddish-blue | ——— |
| *p*-Aminobenzoic acid + aminohydroquinone-methyl ether | Orange | Reddish-violet | Blue | ——— |
| *m*-Aminobenzoic acid + 4-nitro-2-anisidine | Greenish-yellow | Reddish-orange | Red | |
| *m*-Aminobenzoic acid +1, 2-aminonaphthol ether | Red | Greenish-blue | Bluish-green | |
| *m*-Aminobenzoic acid +*a*-naphthylamine | Reddish-orange | Reddish-violet | Reddish-blue | |

He obtained a yellow on acetate silk by treating the fiber with an aqueous suspension of Developer Z (phenylmethylpyrazolone), prepared by adding alcohol to the aqueous solution of the developer. The goods are then washed and passed through diazotized *p*-nitroaniline solution. The same result, except that the shade is weaker, is obtained by treating the acetate silk with an aqueous solution of the Developer Z, instead of the suspension.

Green, olive, and brown shades on acetate silk were obtained by Pokorny[7] by working in an aqueous suspension, prepared by alcohol, of *B*-naphthol, *a*-naphthol, dihydronaphthalene, etc. On treating this with a solution containing sodium nitrite and hydrochloric acid, the corresponding nitroso compound is formed. After washing again, the goods are passed through an aqueous solution of any salt of iron, cobalt, nickel, copper, or chromium. The resulting colors are very fast to soap.

### *The "Fast Bases," Naphthols, and "Rapid Fast" Dyes on Acetate Silk*

Experiments by the author indicate that certain of the Fast Bases, such as those marketed by the Griesheim Elektron Company and others, are applicable to acetate silk under the proper conditions. These bases may be diazotized and developed on the fiber with suitable developers, as for instance the naphthols AS. L. B. Holliday & Company[4] mentions that Fast Red Base, Fast Scarlet Base, Orange Base, etc., may be applied to acetate silk and suggest Method No. 57 for their application. It is possible that some of the Rapid Fast dyes may be applicable for printing acetate silk. These Rapid Fast dyes are faintly alkaline mixtures of stabilized diazo compounds and various naphthols.

The composition of these Fast Bases,[5] according to Rowe is given in Table XXXII. The composition of the naphthols AS of Griesheim Elektron are given in Table XXXIII. Certain of these naphthols also appear to have some affinity for acetate silk. Table XXXIV gives the composition of the Rapid Fast dyes and Table XXXV of some Fast Salts. Rowe[5] also gives tables showing the colors obtained by coupling a wide variety of bases with the various naphthols, etc. While these tables were prepared primarily for the identification of the various amines, they give some idea as to the color obtained on the fiber from these products.

*Method No. 57: The Fast Bases on Acetate Silk.* These bases may be applied at about 32° C. (90° F.) in the presence of hydrochloric acid, until equilibrium is reached. The exhaustion is completed by the addition of sodium acetate, to neutralize the mineral acid present, and by raising the temperature to 65° C. (150° F.). The diazotization and development may be affected by the methods given for the special developed dyes on acetate silk.

### *Hydrogen Ion Concentration in Coupling*

Before closing this part of the subject, it may be well to point out the importance of the hydrogen ion concentration of the coupling bath, in the development of colors on the fiber. Very possibly this subject is even more important in the production of the azo dyes in dyestuff manufacture. It is understood that some of the

European dyestuff manufacturers give this phase of the subject considerably more attention than it receives in America. In coupling on the fiber a proper control of the hydrogen ion concentration, along with the suitable control of other factors, of course, gives much better results in the matching of shades, as well as a considerable economy in the use of the component materials, as it gives a practically complete coupling of the constituents.

TABLE XXXII
THE COMPOSITION OF THE "FAST BASES"

| *Base* | *Composition* |
|---|---|
| Fast Orange R base (Gr.E) | *m*-nitroaniline |
| Fast Garnet B base (Gr. E.) | *a*-naphthylamine |
| Fast Garnet G base (Gr.E.) | *o*-aminoazotoluene |
| Fast Red B base (Gr.E.) | 5-nitro-2-aminoanisole |
| Fast Red BB base (Gr.E.) | *o*-anisidine |
| Fast Red G base (Gr.E.) | 3-nitro-4-aminotoluene |
| Fast Red GL base (Gr.E.) | 3-nitro-4-aminotoluene |
| Fast Red 3GL base (Gr.E.) | 2-nitro-4-chloroaniline |
| Fast Red 3GL base Special (Gr.E.) | 2-nitro-4-chloroaniline |
| Fast Red R base (Gr.E.) | 4-chloro-2-aminoanisole |
| Fast Red RL base (Gr.E.) | 5-nitro-2-aminotoluene |
| Fast Scarlet G base (Gr.E.) | 4-nitro-2-aminotoluene |
| Fast Scarlet R base (Gr.E.) | 4-nitro-2-aminoanisole |
| Fast Blue B base (Gr.E.) | dianisidine |
| Fast Black LB base (Gr.E.) | 2-ethoxybenzeneazo-*a*-naphthylamine |
| Fast Yellow G base (Gr.E.) | *o*-chloroaniline |
| Fast Red base GL (JWL) | 3-nitro-4-aminoanisole |
| Fast Red GL base (Gr.E.) | 3-nitro-4-aminoanisole |
| Fast Red base RL (JWL) | 5-nitro-2-aminotoluene |
| Fast Red RL base (Gr.E.) | 5-nitro-2-aminotoluene |
| Fast Scarlet GL base special (JWL) | 4-nitro-2-aminotoluene |
| Fast Scarlet G base (Gr.E.) | 4-nitro-2-aminotoluene |
| Fast Scarlet base GCL (JWL) | 4-nitro-2-aminotoluene hydrochloride |
| Fast Scarlet GC base (Gr.E.) | 4-nitro-2-aminotoluene hydrochloride |
| Fast Scarlet base 2GL (JWL) | 2, 5-dichloroaniline |
| Fast Scarlet GG base (Gr.E.) | 2, 5-dichloroaniline |
| Fast Yellow base GL (JWL) | *o*-chloroaniline |
| Fast Yellow G base (Gr.E.) | *o*-chloroaniline |
| Fast Yellow base GCL (JWL) | *o*-chloroaniline hydrochloride |
| Fast Yellow GC base (Gr.E.) | *o*-chloroaniline hydrochloride |
| Fast Orange G base (Gr.E.) | *m*-chloroaniline |
| Fast Red KB base (Gr.E.) | 4-chloro-2-aminotoluene hydrochloride |
| Fast Red TR base (Gr.E.) | 5-chloro-2-aminotoluene hydrochloride |
| Fast Scarlet TR base (Gr.E.) | 6-chloro-2-aminotoluene hydrochloride |

TABLE XXXIII
COMPOSITION OF THE NAPHTHOLS AS (GR.E.)

| *Naphthol* | *Composition* |
|---|---|
| Naphthol AS | *B*-hydroxynaphthoic acid anilide (also formerly called BS or AN) |
| Naphthol AS-BS | *B*-hydroxynaphthoic acid *m*-nitroanilide |
| Naphthol AS-RL | *B*-hydroxynaphthoic acid *p*-anisidide |
| Naphthol AS-SW | *B*-hydroxynaphthoic acid *B*-naphtholide |
| Naphthol AS-G | diacetoacetotoluide |
| Naphthol AS-BR | *B*-hydroxynaphthoic acid dianisidide |
| Naphthol AS-TR | *B*-hydroxynaphthoic acid 5-chloro-*o*-toluidide |
| Naphthol AS-D | *B*-hydroxynaphthoic acid *o*-toluidide |
| Naphthol AS-BO | *B*-hydroxynaphthoic acid *a*-naphthalide |

TABLE XXXIV
COMPOSITION OF "RAPID FAST" DYES (Gr.E.)

| | |
|---|---|
| Rapid Fast Red B | Mixture of nitrosamine of diazotized 5-nitro-2-aminoanisole and naphthol AS. |
| Rapid Fast Red BB | Mixture of same nitrosamine and naphthol AS-BS. |
| Rapid Fast Red GG | Mixture of nitrosamine of diazotized *p*-nitroaniline and naphthol AS. |
| Rapid Fast Brown B powder | Mixture of Rapid Fast Red GG and a shading compound. |
| Rapid Fast Red 3GL | Mixture of nitrosamine of diazotized *o*-nitro-*p*-chloroaniline and naphthol AS. |
| Rapid Fast Blue powder | Mixture of naphthol AS and probably tetrazotized dianisidine. |
| Rapid Fast Red GZ | Mixture of diazotized 2,4-dichloroaniline and naphthol AS. |
| Rapid Fast Orange RG | Mixture of nitrosamine of diazotized *o*-nitroaniline and naphthol AS. |
| Rapid Fast Red GL | Alkaline paste of nitrosamine of diazotized *m*-nitro-*p*-toluidine and naphthol AS. |

TABLE XXXV
COMPOSITION OF THE "FAST SALTS" (GR.E.)

| | |
|---|---|
| Fast Red Salt B | stabilized diazotized 5-nitro-2-aminoanisole |
| Fast Red Salt GG | stabilized diazotized 2, 5-dichloroaniline |
| Fast Red Salt GL | stabilized diazotized 3-nitro-4-aminotoluene |
| Fast Scarlet Salt R | stabilized diazotized 4-nitro-2-aminoanisole |

### *The Developed Color Patents*

One of the earliest patented methods of dyeing acetate silk was German Patent No. 199,559, February 19, 1907, to Knoll and Company. French Patent No. 383,636, November 6, 1907; Brit-

ish Patent No. 24,284, November 2, 1907; and United States Patent No. 961,241, June 14, 1910, cover the same process. In these patents it was suggested to dye acetate silk with developed colors by the aid of solvents or swelling agents, as discussed under the solvent methods of dyeing acetate silk, Chapter XVIII.

In United States Patent No. 979,966, December 27, 1910, to E. Knoevenagel, the inventor suggests the use of aqueous solutions of phenol, *B*-naphthol, *p*-aminophenol, etc., and coupling with diazonium salts, in the dyeing of acetate silk. In United States Patent No. 1,002,408, September 5, 1911, to the same inventor, he suggests treating the fiber with an aqueous solution of an aromatic amine, as for instance aniline, *p*-nitroaniline, *a*-naphthylamine, aminoazobenzene, benzidine or *p*-aminophenol, to constitute one component of a dye formed on the fiber.

R. Clavel in British Patent No. 187,964, October 27, 1921, covers the production of azo colors on acetate silk by adding soluble salts to dye baths containing the parent amine, the developer, or to both. Chlorides of ammonium, sodium, potassium, barium, calcium, magnesium, zinc, or tin; or sulfates of sodium, potassium, or magnesium are given as suitable salts. Protective colloids, such as gelatin, silk boil-off liquor, Turkey-red oils, albumin, tannates, soaps, etc., may also be added when the bases or developers are used in neutral or alkaline baths. These assistants allow the use of baths of lower alkalinity and give a greater absorption of the color constituent.

For example, a kilogram of acetate silk may be dyed black by soaking it for 30 to 45 minutes at 60° C. (140° F.) in 20 to 25 liters of a solution containing 25 grams of dianisidine hydrochloride, 50 grams of magnesium chloride, and 40 grams of sodium bicarbonate, and washing. It is diazotized in a bath containing 50 grams of sodium nitrite and 200 cubic centimeters of concentrated hydrochloric acid for 30 minutes at 15° C. (59° F.) and developed in a 20 or 25 liter bath containing 20 grams of *a*-naphthylamine hydrochloride, 8 grams of sodium bicarbonate and 50 grams of magnesium chloride for 1 hour at 65° C. (149° F.). It is then washed, diazotized as before, and soaked for an hour at 65° C. (149° F.) in a slightly alkaline bath containing 20 liters

of water, 5 liters of boil-off liquor, 30 grams of 5-hydroxy-*a*-naphthylamine, and 50 grams of magnesium chloride, whereby the black shade is developed. A final soaping at 60° C. (140° F.) is given. United States Patent No. 1,549,906, August 18, 1925, to the same inventor, appears to cover about the same process. Also see British Patents No. 176,535, No. 182,830, No. 187,964, No. 199,754 and No. 204,179.

*The Two Bath Process*

In British Patent No. 199,754, January 5, 1922, and United States Patent No. 1,571,320, February 2, 1926, to R. Clavel, he suggests in applying the developed colors to acetate silk, that (*a*) the base and developer may be applied in the same bath and then diazotized in a second bath; or (*b*) the base may be applied and diazotized in the one bath, developing in the second bath; or (*c*) the base may be applied in one bath, and then diazotized and developed in the second bath, in the presence of a suitable protective colloid, such as gelatin, silk boil-off liquor, etc. For example, one kilogram of acetate silk may be dyed a brownish-red shade by working it for a half hour at room temperature in a bath containing 25 liters of water, 20 grams of aminoazobenzene, 30 grams of *B*-naphthol, 5 grams of Capri Blue (for shading) and 2 liters of silk boil-off liquor; afterwards adding 50 grams of magnesium chloride and working for one-half hour at 60° C. (140° F.). It is then washed, diazotized cold in a bath containing 20 liters of water, 50 grams of sodium nitrite and 100 cubic centimeters of concentrated hydrochloric acid.

Another example specifies a 25 liter bath containing 20 grams of aminoazotoluene and 2 liters of silk boil-off liquor. After working for 30 minutes, 50 cubic centimeters of sulfuric acid and 50 grams of sodium nitrite are added. Wash and develop in a 60° C. (140° F.) bath containing 25 liters of water, 30 grams of *B*-naphthol and 50 grams of soap.

Burgess, Ledward & Company and W. Harrison obtained British Patent No. 193,646, February 4, 1922, on a single bath process of forming azo colors on acetate silk. In this process the silk is steeped in a bath containing the amino or/and phenolic com-

ponents of the color, subsequently adding sodium nitrite and then acid, whereby the color is developed. Temperatures between 30 and 80° C. (86 to 176° F.) are specified and when the resulting dye tends to form a precipitate in the bath, a protective colloid, such as gelatin or starch is added. These colors may be topped with basic or other dyes.

For example, a red color is obtained on 100 parts of acetate silk by treating it at 60° C. (140° F.) in a bath of 4000 parts of water, containing 2 parts of aminoazobenzene dissolved in 2 parts of hydrochloric acid. After 30 minutes, 10 to 20 parts of sodium acetate are added to aid the exhaustion, and after a further 30 minutes, 2 parts of glue dissolved in water, and 2 parts of *B*-hydroxynaphthoic acid dissolved in water containing 2 parts of ammonia. After a further 15 or 20 minutes, 0.7 part of sodium nitrite and 10 parts of formic acid are added, the temperature being maintained at 60° C. (140° F.). Finally a further 0.7 part or more of sodium nitrate is added, whereby the silk develops a full red shade, which may be topped with Butter Yellow or Nile Blue.

A navy blue on 100 parts of acetate silk may be obtained by treating it in a bath containing 2 parts of dianisidine, 2 parts of 36° Tw. hydrochloric acid and 4000 parts of water at 50 to 70° C. (122 to 158° F.) for 15 minutes. Two parts of glue dissolved in hot water, and 4 parts of *B*-hydroxynaphthoic acid dissolved in 20 parts of hot water containing 2 parts of 0.88 sp. gr. ammonia are added, and in 15 or 20 minutes 1.2 parts of sodium nitrite in 4 parts of water and 15 parts of 90 per cent formic acid are introduced. After working for 30 minutes, 1.2 parts more of sodium nitrite are added and the treatment continued for another 30 minutes. A black shade is obtained from 1-aminobenzene-4-azo-dimethylaniline and *B*-hydroxynaphthoic acid. The dyeings may be made purer and clearer by an after-treatment with reducing agents, such as formaldehyde-hydrosulfite or stannous chloride in acid solution.

In British Patent No. 204,179, July 28, 1922, R. Clavel states that in the production of azo colors on the acetate silk fiber, the development may be effected at temperatures of from 60° C.

(140° F.) to boiling (100° C. or 212° F.) and that the application of the bases may take place at the same high temperatures. The bases and developers may be applied in separate baths or in a combined bath, the diazotization taking place in a separate bath at ordinary or low temperatures. Readily hydrolyzable salts of strong bases, such as sodium acetate, or free bases such as sodium hydroxide, may be added to the base baths, and acids or acid salts, such as hydrochloric or acetic acids or sodium hydrogen phosphate, to the developing baths. Protective colloids such as gelatin, silk boil-off liquor, or sulfonated fatty acid soaps may be used with these, and soluble salts, such as the chlorides of magnesium, ammonium, zinc or tin may also be added to the baths.

British Patent No. 200,873, which will be considered under the Ionamines, also refers to the development of colors on acetate silk. British Patent No. 202,157 and United States Patent No. 1,498,315, discussed under the acid dyes, cover the application to acetate silk of carboxylated aminoazo dyes, which may be diazotized on the fiber and developed. British Patent No. 214,112, discussed under the vat dyes, covers the diazotization and development of dyes on the fiber which were applied from an alkaline hydrosulfite vat. British Patent No. 224,359, under the dispersol dyes, covers the application of many bases by the dispersol process. Also see British Patent No. 245,790.

British Patent No. 231,455, March 31, 1924, to the Society of Chemical Industry, Basle, states that acetate silk may be dyed fast shades of violet, green, and blue to black with monoazo dyes containing at least one diazotizable amino group, then diazotizing on the fiber and developing with an alkyl- or aralkyl-*a*-naphthylamine. For example, ten parts of acetate silk are dyed with 5 per cent of the dyestuff from diazotized *o*-chloroaniline and *a*-naphthylamine-2-sulfonic acid. The material is then washed, diazotized, washed again, and developed in a bath containing 3 per cent of an alkyl-*a*-naphthylamine on the weight of the goods, whereby it is dyed a blue-black shade of excellent fastness.

French Patent Application No. 25,785, of 1924, covers the application of a developed black on acetate silk by a rather involved process. A kilogram of acetate silk is treated for 30 or 45 min-

utes in a 25 liter bath containing 20 grams of dianisidine salt, 50 grams of magnesium chloride and 40 grams of sodium bicarbonate. The impregnated fiber is washed, first in soft water, followed by hard water. The diazotization is affected in a 20 liter bath containing 50 grams of sodium nitrate and 200 grams of hydrochloric acid. The diazotized material is developed for an hour in a bath containing 20 grams of naphthylamine hydrochloride and 8 grams of sodium bicarbonate, after which it is washed. Replace the goods in the developing bath for some time, rewash, and treat for an hour in a 20 liter bath containing 5 liters of filtered soap solution, 35 grams of aminonaphthol (gamma acid), and 50 grams of magnesium chloride. A final washing with water at 60° C. (140° F.), followed by a soap washing, concludes the treatment. Also see British Patent No. 187,964 above.

German Patent No. 428,176, March 1, 1924, to K. H. Meyer and H. Hopff assigned to the I. G. Farbenind. A.-G., acetate silk may be dyed in shades fast to washing by means of slightly water-soluble, feebly basic nitroarylamines or their derivatives. Suitable orange-yellow, greenish-yellow, rddish-yellow, and yellow dyes are 8-nitro-2-naphthylamine, 3-nitro-4-aminobenzophenone, 4-nitro-2-aminodiphenylamine, and the condensation product of 3-chloro-6-nitroaniline and formaldehyde.

### *Oxidized Blacks on Acetate Silk*

Briggs,[6] in an excellent review of the subject of dyeing acetate silk up to 1921, states that the affinity of acetate silk for the aromatic amines makes it especially adaptable for aniline black dyeing.

*Method No. 58: Aniline Black on Acetate Silk.* The acetate silk is treated with a dilute aqueous solution of aniline hydrochloride and then impregnated with strong aniline hydrochloride, chlorate, and copper liquor. It is then whizzed, hung up, and oxidized for an hour or an hour and a half at 40 to 60° C. (104 to 140° F.), after-treated with acid bichromate, and shaded up.

In United States Patent No. 1,448,432, R. Clavel states that aniline black can be brought into acetate silk either direct or in suspended form, but better by impregnating the fiber with aniline hydrochloride and developing. Practical application of this latter

method (impregnation) has shown, in spite of its economy, that the fiber is sometimes injured and the process is not entirely satisfactory. He has therefore superceded this method by United States Patent No. 1,547,789 and British Patent No. 194,840

British Patent No. 194,840, January 5, 1922, and United States Patent No. 1,547,789, July 28, 1925, to R. Clavel, cover a process for obtaining black shades on acetate silk by means of Diphenyl Black Base (*p*-aminodiphenylamine). The affinity of this fiber for amino, imino and acidylamino compounds is utilized by impregnating the fiber with Diphenyl Black Base, in the presence of an acid, such as acetic acid, and a soluble chloride, with or without protective colloids, and then oxidizing the base on the fiber.

*Method No. 59: Black on Acetate Silk with Diphenyl Black Base.* A stock solution is prepared containing 200 grams of Diphenyl Black Base, 500 cubic centimeters of 80 per cent acetic acid and 500 cubic centimeters of water. For 1 kilogram of acetate silk, take 250 cubic centimeters of the above stock solution in 20 liters of water and 2 liters of silk boil-off liquor. Heat the bath to 50° C. (122° F.) and work the goods for an hour. Add 50 grams of sodium acetate and work the material for another hour at 60° C. (140° F.). Rinse and oxidize by the addition of three portions of 25 grams each of sodium perborate, at intervals of 20 minutes, after which the goods may be washed or brightened. The perborate may be replaced by hypochlorite or ammonium persulfate.

*Method No. 60: Black on Acetate Silk with Diphenyl Black Base.* Another method covered by the same patent utilizes stock solutions (*A*) containing 200 grams Diphenyl Black Base, 550 cubic centimeters of 50 per cent acetic acid and 250 cubic centimeters of 50 per cent lactic acid made up to 1250 cubic centimeters; and (*B*) containing 125 grams of 30° Be. (sp.gr. 1.26) aluminum chloride, 125 grams of 30 Be. chromium chloride, 20 grams of 40° Be. (sp. gr. 1.38) cupric chloride and 150 grams of sodium chlorate in each 1250 cubic centimeters. Seven hundred and fifty cubic centimeters each of *A* and *B* are mixed and diluted to 4.5 to 6.5 liters, and the acetate silk steeped in this bath, cold, turning the goods two or three times. Remove the goods from the bath,

hydroextract, dry and age for an hour at 80° C. (176° F.). Wash and soap at 50 to 60° C. (122 to 140° F.), rinse well and finally sour. About 12 per cent of Diphenyl Black Base, on the weight of the goods, is necessary for a good black. Also see United States Patent No. 961,241 covering aniline black and other methods.

Pokorny[7] prepared Aniline Black on acetate silk by working the goods for a few minutes in a fine aqueous suspension of 10 grams of Diphenyl Black Base I (M.L.B.) in 10 liters of water. After washing, the black is developed by working the well squeezed or hydroextracted goods for a few minutes in an oxidizing solution. This oxidizing solution contains 10 grams of ammonium chloride, 10 grams of sodium chlorate and 200 grams of vanadium solution in 10 liters of water. The vanadium solution is prepared by heating 10 grams of ammonium vanadate and 100 cubic centimeters of 34° Tw. hydrochloric acid on a water bath with 400 cubic centimeters of water until it is completely dissolved to form a green solution. Five cubic centimeters of glycerol are then added and the solution treated until the color changes to blue. This is diluted to 10 liters with water. The goods are again squeezed and steam oxidized with saturated steam, without pressure. With the dilute solutions mentioned above, repeated treatments are necessary to obtain the deepest blacks.

British Patent No. 255,962, to the British Celanese Company and G. H. Ellis states that processes involving the oxidation of aniline, *p*-aminophenol, *p*-phenylenediamine, *p*-aminodiphenylamine,. benzidine, tolidine, *α*-naphthylamine, or other amino compounds may be used on acetate silk by absorption of the base from aqueous solutions or dispersions, followed by treatment with a suitable oxidizing agent. The amino impregnated fiber is rinsed and impregnated with suitable oxidizing agents, such as chlorates, hypochlorites, or bichromates. These may be used in conjunction with such catalysts as the salts of vanadium, iron, and copper, and such soluble salts as sodium sulfate, or the chlorides of ammonium, barium, calcium, and magnesium may be added. Sodium or calcium acetate may be added to the solution of the organic base, when it is used in the form of an acid salt liable to cause tendering. After drying, the material is aged in an atmosphere of warm moist air.

The inventors state that in the past some of the oxidized colors on acetate silk have not been very satisfactory, due to the frequent blinding of the fiber and crocking of the color. This rubbing occurred when both the one- and two-bath dyeing processes were used. However, they find that when the amino compound is applied to the acetate silk by the usual dispersol process (see Chapters XXI to XXIII) the absorption is more gradual, and better results, as regards to rubbing, are obtained.

For example: ten pounds of acetate silk in hanks may be dyed a full deep black by dissolving 0.75 pound of *p*-aminodiphenylamine base in 6 pounds of 50 per cent Turkey-red oil, diluting with water and heating to 80° C. (176° F.) for a short time to effect solubilization or dispersion. This is diluted with hot water and added through a filter cloth to a 25 gallon dye bath at 80° C. The acetate silk is entered at this temperature and worked for 2 hours. After rinsing with soft water the goods are impregnated cold with their own weight of an oxidizing solution prepared as follows: Dissolve 2 parts of gum tragacanth in 300 parts of water; 8 parts of chromium chloride in 56 parts of water; 4 parts of aluminum chloride in 50 parts of water; 3 parts of cupric chloride in 50 parts of water; and 60 parts of sodium chlorate in 120 parts of water. Add water to 1000 parts. The goods are now aged, preferably after drying at a moderate temperature, for 5 minutes in a steam ager, and washed off in hot water or very dilute formic acid (about one cubic centimeter per liter) to remove mineral matter. The yarn has now acquired a dead black color, the luster and handle being unimpaired, and may be dried and finished as required.

In another example, the same weight of yarn is dyed a medium brown shade by 0.5 pound of benzidine. This is dispersed or dissolved as above with 2.5 pounds of dispersing agent prepared by sulfonating a mixture of naphthalene and oleic acid (Twitchell reagent). This is diluted with soft boiling water and filtered into the 25 gallon dye bath. The goods are entered, the temperature raised to 70 or 75° C. (158 or 167° F.) in about 45 minutes and worked at this temperature for an hour. They are then rinsed and the base oxidized by the impregnation and ageing process

given in the previous example. After rinsing in the dilute formic acid bath, the goods are a dull brown shade.

In the same manner a fawn-brown shade may be obtained with 0.5 pound of *p*-aminophenol at 70 to 75° C., and oxidizing as above.

One-half pound of *p*-phenylenediamine at the same temperature is used to obtain a deep brown color. After rinsing, the goods are impregnated with a bath made up as follows: Two parts of gum-tragacanth in 300 parts of water; 4 parts of aluminum chloride in 50 parts of water; 3 parts of cupric chloride in 50 parts of water; and 150 parts of sodium bichromate in 100 parts of water. Add water to make 1000 parts. After squeezing evenly so that the fiber contains only its own weight of the oxidizing mixture, it is aged for 5 minutes in a steam ager and rinsed in very dilute formic acid.

British Patent No. 258,699, July 10, 1925, to the Silver Springs Bleaching and Dyeing Company and A. J. Hall states that acetate silk may be dyed in very fast black shades by the application of 2,-4-diaminodiphenylamine from aqueous solutions or suspensions and subsequent immersion in hot or boiling aqueous solutions of oxidizing agents (see British Patent No. 246,879). Or the goods may be impregnated with a paste containing an oxidizing agent, a catalyst, an acid, and 2,4-diaminodiphenylamine followed by exposure to a moist warm atmosphere for development of the black color. Mixtures containing 2,4-diaminodiphenylamine and one or more aromatic amines, such as aniline, *o*-toluidine, *p*-phenylenediamine, and *p*-aminodiphenylamine may be used. Ferric chloride, permanganates, chlorates, perborates, hydrogen peroxide, and bromine are mentioned as suitable oxidizing agents. The oxidation of 2,4-diaminodiphenylamine on acetate silk will take place by exposure to air alone, giving a full black, even in the absence of light.

For example, 10 parts of acetate silk are immersed for an hour at 40.5° C. (105° F.) in a bath containing 0.75 part of 2,4-diaminodiphenylamine, 0.6 part of soap, 0.6 part of 0.920 sp. gr. ammonia and 300 parts of water. It is then rinsed in warm water and immersed for a half hour at 65.5 to 71° C. (150 to 160° F.) in a bath containing 4 parts of sodium chlorate, 25 parts of hydro-

chloric acid, 1 part of copper sulfate, and 300 parts of water, then rinsed in warm water, soaped at 60° C. (140° F.), rinsed in warm water and dried.

*References*

[1] E. Greenhalgh, *Dyer and Calico Printer 55,* 146 (1926).
[2] R. G. Dort, *American Dyestuff Reporter 15,* 266 (1926).
[3] W. E. Sanderson, *J. Soc. Dyers and Colourists 38,* 162-5 (1922).
[4] L. B. Holliday & Company, "Application and Properties of Dyestuffs," p. 94.
[5] F. M. Rowe, *J. Soc. Dyers and Colourists 37,* 204-15 (1921); *40,* 218-30 (1924); *41,* 354-6 (1925); *42,* 82-3 (1926).
[6] J. F. Briggs, *J. Soc. Dyers and Colourists 37,* 287-96 (1921).
[7] J. Pokorny, *J. Soc. Dyers and Colourists 42,* 345-8 (1926).

# CHAPTER XVII

# SPECIAL COMPONENTS FOR THE DEVELOPED OR AZOIC COLORS ON ACETATE SILK

*The Acedronoles, Acetylines, Azoniles, Azonines, Azoics, Azoles, Silkons, and Other Special Azoic Color Components on Acetate Silk.*

WHILE the products to be discussed in this chapter do not have a very wide use upon acetate silk at the present time owing to the greater ease of application of the many new dyes originated especially for use upon acetate silk, they are still used to some extent for special purposes. As mentioned in Chapter XVI, most of the products under discussion here are in reality well-known bases, amines, phenols, etc., which have more or less use for the other purposes in the dyestuffs or dyeing industry, either as dyestuff components or intermediates, or in the development of similar colors on other fibers. However, their methods of application to acetate silk are usually quite different from their application to other fibers, such as cotton. The principal justification for including a chapter on these products in the present volume is that at the present time the developed blacks are the most satisfactory offered for acetate silk, and that the developed colors are used to some extent for very fast and heavy shades on hosiery, etc.

## *The Acedronoles*

The Acedronoles of the Badische Company belong to the class of products under discussion. These products are applied to the scoured but unsaponified acetate silk by Method No. 61. Method No. 61-A covers the diazotization, and No. 61-B the development. Table XXXVI gives a list of the colors obtained, the developers used, and the amount of sodium acetate, where this is required. Most of these combinations leave the cotton of acetate silk-cotton unions either white or only slightly stained and are therefore suited

for two color combinations on acetate silk-cotton unions. However formulas No. X7, No. X8, No. X32, No. X33 and No. X43 stain cotton and the regenerated rayons considerably.

Acedronoles AB, AN, AT, BN, BT, CA, and ND are available both as 30 per cent pastes and in powder form, while B, DA, and T are in the form of 30 per cent pastes. In preparing the Acedronole dye bath the Acedronoles B, BT, DA, and T are dissolved in hot water without any addition. Acedronoles AN, BN, CA and ND are wet-out with 50 to 100 times their weight of boiling water and dissolved by the addition of double their weight of concentrated hydrochloric acid. In other words, each pound of Acedronoles AN, BN, CA, and ND is mixed with 6 to 12 gallons of boiling water and then 2 pounds of hydrochloric acid is added to complete the solution.

Acedronole AB is dissolved by mixing it with 10 times its weight of cold 85 per cent formic acid, adding about 100 times its weight of boiling water, and then about 4 volumes of concentrated hydrochloric acid, to complete the solution. In other words, each 100 grams (about 3.5 ounces) of Acedronole AB should be mixed with a liter (slightly over a quart) of formic acid, adding about 10 liters (2.7 gallons) of boiling water, and after stirring well, 400 cubic centimeters (about 13.8 fluid ounces) of hydrochloric acid.

Acedronole AT is dissolved in exactly the same way as Acedronole AB, except that just twice the amount of hydrochloric acid given for AB is used. In other words, for 100 grams of AT, use 1 liter of formic acid, 10 liters of boiling water and 800 cubic centimeters (about 27.5 fluid ounces) of concentrated hydrochloric acid.

Acedronoles ND, CA, BN, AN, DA, T and B may be mixed together in any proportions in the dye bath and Acedronoles AB and AT may also be used together, but should not be mixed with the above on account of the difference in the acidity of their baths, which may cause precipitation of the Acedronoles AB and AT in the less acid bath. Sodium acetate is not used with Acedronoles AB, AT, and BT.

*Method No. 61: The Acedronoles on Acetate Silk.* The dye

bath is prepared by straining the above Acedronole solution through cotton into the 20 to 1 dye bath at about 40° C. (104° F.). The scoured acetate silk is entered at this temperature and worked for about 15 minutes. The temperature is raised to 60 or 70° C. (140 or 160° F.) and the handling continued for about a half-hour. Where required, as given in Table XXXVI, the stated quantity of sodium acetate, in solution, is then slowly added to the bath to aid exhaustion. After a further working for about a half-hour, a rinse of cold water is given and the acetate silk is ready for diazotization.

*Method No. 61-A: Diazotizing the Acedronoles.* The diazotizing bath for heavy shades is prepared cold with 4 per cent of sodium nitrite and 10 per cent of concentrated hydrochloric acid. For light shades a bath of half this strength is sufficient. The impregnated acetate silk is treated cold, worked well, rinsed, and developed immediately.

Phenol, resorcinol, *a*- and *B*-naphthol, Developer BON and Oxamine Developer B are recommended for use with the Acedronoles. The phenol or resorcinol developing bath is prepared by dissolving the developer directly in hot water, without any other addition. The naphthols and Developer BON are first made into a paste with hot water and an equal quantity of 38 or 40° Be. sodium hydroxide solution, and this paste dissolved by adding hot water. Oxamine Developer B is dissolved in hot water by the addition of a little hydrochloric acid.

*Method No. 61-B: Developing the Acedronoles.* The rinsed acetate silk, fresh from the diazotizing bath, is entered into the cold developing bath, except in the case of Developer BON which is used at 60 to 70° C. (140 to 158° F.) instead of cold, and worked for about a half hour. In using Developer BON, 2 to 4 cubic centimeters of 6° Be. acetic acid, per liter of developing bath, must be added so as to give the liquor an acid reaction to litmus paper. After development the goods should be rinsed well and may be scrooped in the usual manner. A warm soaping in a bath containing 2 or 3 grams per liter of olive oil soap will increase the luster of the rayon.

TABLE XXXVI

THE ACEDRONOLES ON ACETATE SILK

| Formula No. | Color | Base | Developer |
|---|---|---|---|
| X1 | Yellow | 1% Acedronole AB | 1.5% phenol |
| X2 | Reddish-orange | 1% Acedronole AB | 1.5% resorcinol |
| X3 | Orange-red | 1% Acedronole AB | 1.5% *B*-naphthol |
| X4 | Henna | 1% Acedronole AB | 1.5% *a*-naphthol |
| X5 | Cardinal | 0.7% Acedronole AB | 3% Developer BON |
| X6 | Dark cardinal | 1% Acedronole AB | 1.5% Oxamine Developer B |
| X7 | Brown | 1% Acedronole ND with 5% sodium acetate | 1% resorcinol |
| X8 | Darker brown | 1.5% Acedronole DN with 6% sodium acetate | 1.5% resorcinol |
| X9 | Orange scarlet | 2% Acedronole CA with 6% sodium acetate | 1.5% resorcinol |
| X10 | Bright scarlet | 1% Acedronole CA with 4% sodium acetate | 2% Developer BON |
| X11 | Darker scarlet | 1.5% Acedronole CA with 6% sodium acetate | 3% developer BON |
| X12 | Orange | 1.25% Acedronole BN with 6% sodium acetate | 1.5% resorcinol |
| X13 | Dark orange | 1.25% Acedronole BN with 6% sodium acetate | 1.5% *B*-naphthol |
| X14 | Orange brown | 1% Acedronole AN with 6% sodium acetate | 1.5% phenol |
| X15 | Darker than X14 | 1.5% Acedronole AN with 8% sodium acetate | 1.5% phenol |
| X16 | Brown, reddish | 1% Acedronole AN with 6% sodium acetate | 1.5% *a*-naphthol |
| X17 | Darker than X16 | 1.5% Acedronole AN with 8% sodium acetate | 2% *a*-naphthol |
| X18 | Darker than X17 | 1% Acedronole AN with 6% sodium acetate | 1.5% resorcinol |
| X19 | Darker than X18 | 1.5% Acedronole AN with 8% sodium acetate | 2% resorcinol |
| X20 | Darker than X19 (Very Dark) | 1% Acedronole AN with 6% sodium acetate | 1.5% *B*-naphthol |
| X21 | Deep Blue | 1% Acedronole AN with 6% sodium acetate | 2.5% Developer BON |
| X22 | Black | 3% Acedronole AN with 10% sodium acetate | 5% Developer BON |
| X23 | Yellow | 1% Acedronole AT | 1.5% phenol |
| X24 | Reddish-tan | 1% Acedronole AT | 1.5% resorcinol |
| X25 | Bright Red | 1% Acedronole AT | 1.5% *B*-naphthol |
| X26 | Darker and Browner than X4 | 1% Acedronole AT | 1.5% *a*-naphthol |
| X27 | Cerese | 1% Acedronole AT | 1.5% Oxamine Developer B |
| X28 | Dark Cerese | 0.7% Acedronole AT | 3% Developer BON |

TABLE XXXVI

THE ACEDRONOLES ON ACETATE SILK

| *Formula No.* | *Color* | *Base* | *Developer* |
|---|---|---|---|
| X29 | Medium blue | 1% Acedronole DA 30% paste with 2% sodium acetate | 2% Developer BON |
| X30 | Darker than X29 | 1.5% Acedronole DA 30% paste with 4% sodium acetate | 2.5% Developer BON |
| X31 | Darker than X21 or X30 | 2% Acedronole DA 30% paste with 6% sodium acetate | 3% Developer BON |
| X32 | Blue-black | 6% Acedronole DA 30% paste with 10% sodium acetate | 5% Developer BON |
| X33 | Black | 6% Acedronole DA 30% paste with 10% sodium acetate | 1% phenol |
| X34 | Bright light yellow | 2% Acedronole B 30% paste with 4% sodium acetate | 1.5% phenol |
| X35 | Lighter than X24 | 2% Acedronole B 30% paste with 4% sodium acetate | 1% resorcinol |
| X36 | Red henna | 4.5% Acedronole B 30% paste with 6% sodium acetate | 1.5% resorcinol |
| X37 | Darker than X27 | 6% Acedronole B 30% paste with 6% sodium acetate | 2% *B*-naphthol |
| X38 | Lavender Blue | 2% Acedronole B 30% paste with 4% sodium acetate | 2.5% Developer BON |
| X39 | Darker than X38 | 3% Acedronole B 30% paste with 6% sodium acetate | 3% Developer BON |
| X40 | Slightly darker than X34 | 2.5% Acedronole T 30% paste with 5% sodium acetate | 1.5% phenol |
| X41 | Dark Red | 4% Acedronole T 30% paste with 6% sodium acetate | 2% *B*-naphthol |
| X42 | Red brown or dark henna | 3.5% Acedronole T 30% paste with 6% sodium acetate | 1.5% resorcinol |
| X43 | Dark tan | 1% Acedronole BN and 0.4% Acedronole ND with 6% sodium acetate | 1.5% resorcinol |
| X44 | Darker than X43 | 0.5% Acedronole AN and 0.2% Acedronole BN with 3% sodium acetate | 1% resorcinol |

The Acedronole colors usually have a good fastness to water, washing, dilute organic acids, ironing, and with the exception of formulas No. X6, No. X12, No. X13, No. X37, and No. X41, a good fastness to light. They will withstand cross-dyeing in an acid bath (wool), with the exception of formulas No. X2, No. X3, No. X5, No. X9, No. X10, No. X11, No. X18, No. X19, No. X20, No. X24, No. X25, No. X28, No. X34, No. X35, No. X36, and No. X37.

Where it is desired to dye the other fiber combined with the acetate silk, as in unions, the acetate silk should be dyed first according to Methods No. 61, No. 61-A, and No. 61-B. The cotton is then dyed with such substantive dyes as do not stain acetate silk, at about 40 to 60° C. (104 to 140° F.), or at a maximum of 80° C. (176° F.).

### *The Acetylines*

The Acetylines of the Société Anonyme des Matiers Colorantes et Produits Chimiques belong to the developed class also. They are applied by Method No. 62. Acetylines SA, SB, SH, and SR give direct shades varying from yellow to orange, and Acetyline SP gives a direct brown, as shown in Table XXXVII. The Acetylines may be diazotized on the fiber and developed by Methods No. 62-A and No. 62-B. The acetate silk should not be allowed to remain any longer than necessary in the acid Acetyline bath as acid solutions hydrolyze cellulose acetate to some extent.

*Method No. 62: The Acetylines on Acetate Silk.* The dye bath should be prepared by mixing the Acetyline with half its weight of 20° Be. hydrochloric acid. This paste is dissolved in boiling water, using about 250 parts of water for each part of dye. If hard water is used, it should be slightly acidified with acetic acid. Before entering this bath the acetate silk should be thoroughly wet-out by working for about 5 minutes in a bath containing 5 per cent of ammonia, on the weight of the goods. It is then rinsed with water and finally neutralized with water containing acetic acid. This wet-out silk is then entered at about 15° C. (59° F.) into the 30 to 1 dye bath containing the Acetyline, and the tem-

perature of the bath gradually raised to 50° C. (122° F.) for about 30 minutes.

*Method No. 62-A: Diazotizing the Acetylines.* The acetate silk from the above bath should be rinsed and diazotized at a temperature below 15° C. (59° F.) in a 30 to 1 bath containing 2 to 5 per cent of sodium nitrite and 5 to 10 per cent of 20° Be. hydrochloric acid. In the case of Acetyline SD, the direct color of the Acetyline on the acetate silk must be entirely decolorized in the diazotizing bath. In case this does not occur in the above bath, it must be given a longer or stronger treatment, until the direct color is discharged.

*Method No. 62-B: Developing the Acetylines.* The diazotized acetate silk should be rinsed quickly in cold water and entered into the developing bath without delay. A 30 to 1 developing bath is used containing 1 to 5 per cent of the desired developer and 1 to 2 per cent of acetic acid. The acetate silk is entered at 15° C. (59° F.) and the temperature gradually raised to 50° C. (122° F.), while working for about 45 minutes. After developing, the acetate silk should be rinsed well, brightened, and dyed.

Developers MA and MC are dissolved in boiling water, without any other addition. Developers MB and MP should be mixed with an equal weight of 30° Be. sodium hydroxide solution, and then dissolved in boiling water. However the developing bath should be neutralized with acetic acid before entering the acetate silk. Developer ME is pasted with half its weight of sodium carbonate, dissolved in boiling water and then neutralized as above. Developer ML is mixed with an equal weight of 20° Be. hydrochloric acid, and then dissolved in boiling water.

As most of the Acetylines do not stain other fibers they may be used for two colored effects on unions containing acetate silk. The Acetylines may be mixed in the dye bath, and the developers may be combined with each other in the developing bath to get a wider range of colors. Also the diazotized and developed colors may be "topped" with the direct Acetylines. This is particularly useful for greens and certain blacks. Table XXXVII gives the colors obtained direct and by development, and Table XXXVIII the amounts used to obtain various colors.

## TABLE XXXVII

### Colors Obtained from the Acetylines, Direct and with the Various Developers

| *Acetyline* | *Direct Color* | *Developer* *MA* | *MB* | *MC* | *ME* | *ML* | *MP* |
|---|---|---|---|---|---|---|---|
| SA | Greenish-Yellow | Golden Orange | Reddish-Orange | Orange | Red | Bluish-Red | Reddish-Brown |
| SB | Pure Yellow | Reddish-Yellow | Poncean Red | Orange | Reddish-Violet | Bluish-Red | Copper-Red |
| SC | | Light Yellow | Bluish-Red | Light Orange | Violet | Bluish-Red | Reddish-Brown |
| SD | | Orange | Reddish-Violet | Violet-Brown | Pure Blue | Reddish-Violet | Reddish-Brown |
| SE | | Violet Brown | Brown to Brownish-Black | Violet Brown | Brown to Black | Brown to Dark Violet | Brown |
| SH | Yellow | Pure Yellow | Orange | Yellowish-Orange | Deep Salmon | Yellowish-Red | Copper |
| SL | Light Yellow | Reddish-Yellow | Reddish-Orange | Brownish-Orange | Rose | Light Violet | Copper |
| SM | | Orange Yellow | Orange | Orange Yellow | Reddish-Orange | Orange | Orange |
| SP | Orange Brown | Copper | Violet Brown | Violet Brown | Dark Brown | Dark Violet | Violet Brown |
| SR | Pure Yellow | Greenish-Yellow | Golden Yellow | Golden Yellow | Orange | Salmon | Copper |

TABLE XXXVIII
AMOUNTS OF ACETYLINES AND DEVELOPERS USED

| *Color* | *Per Cent Acetyline* | | *Per Cent Developer* | |
|---|---|---|---|---|
| Orange-Red | 3% | SA | 2% | MB |
| Deep Orange | 3% | SA | 2% | MC |
| Bluish-Red | 3% | SA | 2% | ML |
| Poncean Red | 3% | SB | 2% | MB |
| Bluish-Red | 3% | SB | 2% | ME |
| Bluish-Red | 2% | SC | 2% | ML |
| Reddish-Brown | 2% | SC | 2% | MP |
| Violet | 2% | SC | 2% | ME |
| Violet Brown | 3% | SE | 2% | MC |
| Yellowish-Orange | 3% | SH | 2% | MC |
| Pure Blue | 2% | SD | 1.5% | ME |
| Violet Blue | 0.5 | SD | 2% | ME |
| Greenish-Black | 20% | SE | 5% | ME |
| Greenish | 0.2% | SD | 1.5% | ME, topped with 3% SA |
| Bluish-Black | 5% | SD | 5% | ME, topped with 3% SA |

### *The Azoniles*

The Azoniles of Meister, Lucius, and Bruning are another variety of products for development on acetate silk. Some of these stain the fiber directly, while others leave it colorless until developed. The manufacturers recommend only *B*-naphthol, resorcinol and Dianil Developer O for use upon the Azoniles but probably some of the other developers mentioned previously may be applicable in some cases to give additional shades.

The Azoniles are dissolved for use by mixing into a paste with the necessary quantity of concentrated hydrochloric acid (see Table XXXIX below), adding 100 parts of boiling water to each part of dye, and finally heating to the boil if necessary. Actual boiling of the solution should be avoided in the case of Azonile R, which should simply be made into a paste with the acid, the water added at 90° C. (195° F.) and allowed to stand for 15 minutes at this temperature. Clear solutions will be obtained with Azonile N and SR, which may be stained into the lukewarm dye bath direct. In a 1:100 dilution Azonile N tends to precipitate on cooling, therefore the solution should be very hot when adding it to the dye bath. Azoniles G, R and B leave some residue when dissolving, therefore particular care should be exercised in filtering them.

TABLE XXXIX

AMOUNT OF HYDROCHLORIC ACID REQUIRED TO DISSOLVE THE AZONILES

| To Each 100 Parts of | Use Hydrochloric Acid |
|---|---|
| Azonile B | 60 Parts |
| Azonile G | 70 Parts |
| Azonile N | 60 Parts |
| Azonile R | 100 Parts |
| Azonile SR | 60 Parts |

*Method No. 63: The Azoniles on Acetate Silk.* The scoured goods are entered into a lukewarm 30 or 40 to 1 dye bath, working well and gradually adding during the dyeing from 10 to 20 per cent of ammonium acetate, in solution, to aid exhaustion. In the case of Azoniles G, R and B, the ammonium acetate should be added very gradually in order to prevent precipitation of the Azonile. The temperature is raised during a half-hour to 60 or 70° C. (140 to 160° F.) and the dyeing continued for a half-hour at this temperature, when the bath is usually exhausted.

*Method No. 63-A: Diazotizing of the Azoniles.* The thoroughly rinsed goods are diazotized in a cold 20 to 1 bath for 30 minutes, containing 2 to 5 per cent of sodium nitrite and 4 to 10 per cent of concentrated hydrochloric acid, on the weight of the goods, depending upon the depth of shade. They are then rinsed well and should be immediately developed. In case a standing bath is used for diazotizing, it should be replenished after each run with about one-third the original quantity of acid and nitrite. The same proportion of developer should be added to the developing bath if a standing bath is used.

The developers are dissolved in hot water. In the case of *B*-naphthol, the developer is pasted with 70 parts of 77° Tw. sodium hydroxide solution per 100 parts of naphthol, before adding the water. Thirty parts of soda ash are used in the same manner with each 100 parts of Dianil Developer O.

*Method No. 63-B: Developing the Azoniles.* The 20 to 1 developing bath is prepared with 2 to 6 per cent of developer, on the weight of the goods, according to the depth of shade. The goods are entered cold and the bath slowly heated to 49° C. (120° F.), working the goods for about 45 minutes. After developing, the

acetate silk is rinsed well, hydroextracted and dried at not over 49° C. The brilliancy of the color is increased by a light soaping before drying.

The Azoniles give good full shades of excellent fastness to water, and with the exception of Azonile R which turns somewhat yellow, to washing. Azonile G, even when not diazotized and developed, has very good fastness properties. With the exception of Azonile R developed with *B*-naphthol, and particularly Azonile B with Dianil Developer O, all of the Azoniles are very fast to light. Table XL gives a few of the colors obtainable.

TABLE XL

Colors Obtainable with the Azoniles and Various Developers

| *Color* | *Azonile* | *Developer* |
|---|---|---|
| Yellow | G | None, dyed direct |
| Scarlet | G | *B*-napthol |
| Dull Yellow | N | Resorcinal |
| Orange | R | Resorcinol |
| Cerise | R | *B*-naphthol |
| Violet | R | Developer O |
| Bright Blue | B | Developer O |
| Reddish-Brown | SR | Resorcinol |
| Navy Blue | SR | Developer O |
| Black | SR | Developer O |

They may readily be used for two color effects on unions of acetate silk with cotton or/and other rayons, by first applying the Azoniles as described above, which only stain the cotton faintly, and afterwards cross-dyeing at 60 to 70° C. (140 to 160° F.) in a salt bath containing no soap or alkalies with direct cotton colors which do not appreciably stain acetate silk.

### *The Azonines*

The Azonines are the product of the Cassella Company and are applied in two ways, according to Methods No. 64 and No. 65. As a rule they do not stain the cotton of acetate silk-cotton unions, and are therefore useful for two colored effects on goods of this class. Azonine G is directly soluble in boiling water without any addition. The other members of this group either require the addition of hydrochloric acid to bring them into solution, as is

the case with most bases of this class, or they may be applied with the aid of Tetralin or a similar solvent which is soluble in an aqueous soapy dye bath. This latter method probably belongs with the dispersol methods of dyeing. Azonines R, 2R and S may be mixed in any proportions and give direct shades of yellow to orange without development. Azonine G also gives a direct shade and is never developed. All of the other Azonines may be developed. Azonine B is colorless until developed. Table XLII gives a list of the colors obtainable. Azonine 2R may be aminoazotoluene.

Also see Azonine SF which is best applied by dispersol methods and is discussed with the Direct Azonines under the Dispersol Dyes. It may also be applied in a formic acid bath, and in either case is diazotized and developed on the fiber. In using formic acid, the Azonine is pasted with twice its weight of 85 per cent formic acid and then dissolved in hot water. The material is entered into this bath, without any other addition and dyed for about 45 minutes at 70 to 75° C. (157 to 167° F.).

*Method No. 64: The Azonines on Acetate Silk.* When applied by the acid method, Azonines B, R, 2R and S are dissolved in about 100 times their weight of water and the particular quantity of hydrochloric acid given in Table XLI. This solution, or the aqueous solution of Azonine G, is strained into the 30 or 40 to 1 dye bath at 60° C. (140° F.). The scoured material is entered and worked for 45 minutes at 60 to 70° C. (140 to 160° F.). In the case of Azonine G, it is necessary to add from 3 to 10 per cent of acetic acid to the bath to aid exhaustion, and a standing bath may be used to advantage. In dyeing light shades or where there is trouble in leveling, the addition of a little hydrochloric acid to the dye bath, say 0.2 to 0.5 per cent on the weight of the goods, may be advantageous.

TABLE XLI

AMOUNT OF HYDROCHLORIC ACID REQUIRED TO DISSOLVE THE AZONINES

| For Each Pound of | Use Hydrocholric Acid |
|---|---|
| Azonine B | 9.5 ounces |
| Azonine R | 16. ounces |
| Azonine 2R | 13. ounces |
| Azonine S | 9.5 ounces |

*Method No. 65: Azonines B, R, 2R, and S With Tetralin.* One part of the Azonine dyestuff is made into a paste with three parts of tetralin, four and one-half parts of soap, and one-half part of soda ash. This paste is dissolved in 100 parts of boiling water and this solution is sieved into the dye bath after which the dyeing proceeds as in Method No. 64. While the dye exhausts from the bath very well, it may advantageously be used again on account of its tetralin and soap content. When this method is used on acetate silk-cotton unions, both fibers may be dyed in the one dye bath, in which case the salt is not added to the dye bath until twenty or thirty minutes after the goods are entered, by which time most of the Azonine will have been absorbed.

TABLE XLII
COLORS WITH THE AZONINES AND VARIOUS DEVELOPERS

| *Color* | *Per Cent Azonine* | | *Per Cent Developer* |
|---|---|---|---|
| Lemon Yellow (1) | 4% | G | Direct, never developed |
| Golden Yellow (2) | 2% | R | 2% Phenol |
| Reddish-Brown (3) | 2% | R | 2% Resorcinol |
| Bright Scarlet (4) | 2% | R | 2% *B*-Naphthol |
| Dark Red (5) | 2% | R | 2% Developer ON |
| Bright Yellow (6) | 2% | 2R | Direct, not developed |
| Reddish-Brown (7) | 2% | 2R | 2% Resorcinol |
| Lighter than 3 | | | |
| Scarlet (8) | 2% | 2R | 1% *B*-Naphthol |
| Lighter than 4 | | | |
| Scarlet (9) | | | |
| Redder than 4 | 2% | 2R | 2% *B*-Naphthol |
| Deep Maroon (10) | 2% | 2R | 2% Developer ON |
| Dark Blue (11) | 1.5% | B | 3% Developer ON |
| Light Brown (12) | 1% | S | 1% Phenol |
| Very Dark Purple (13) | 1% | S | 1% Resorcinol |
| Purple (14) | 1% | S | 1% Resorcinol |
| Darker and bluer than 13 | | | |
| Gray Blue | 0.2% | S | 1% Developer ON |
| Black | 3% | S | 3% Developer ON |

*Method No. 64-A: Diazotizing the Azonines.* The Azonines, with the exception of Azonine G, may be diazotized on the fiber in a cold bath containing 2 to 4 per cent of sodium nitrite and 5 to 10 per cent of 34° Tw. hydrochloric acid, according to the depth of shade, for 15 or 20 minutes. If preferred, less acid may be used and a little longer time given, for instance 5 or 10 per cent

of 21° Tw. hydrochloric acid may be used cold for 30 minutes, instead of the above. After diazotizing rinse well and develop immediately.

The developers are prepared by dissolving the phenol or resorcinol in hot water. One part of *B*-naphthol is boiled with 2 parts of Turkey-red oil and 20 to 30 parts of water. Developer ON, which is possibly *B*-hydroxynaphthoic acid, is dissolved by boiling with 2 parts of sodium acetate and 20 to 30 parts of water. These solutions are added directly to the developing bath.

*Method No. 64-B: Developing the Azonines.* The color is developed with from 1 to 3 per cent of developer for 20 to 30 minutes at 45 to 60° C. (115 to 140° F.). Azonine B requires about twice as much developer as the other Azonines. The goods should be rinsed and the shades may be brightened by a light soaping.

### *The Azoles*

The Azoles of the Actien-Gesellschaft fur Anilin-Fabrikation are another brand of developed dyestuffs. Azoles AG, AR and AZ give direct shades which are fast enough for some purposes. Azoles 6GL and R also give direct shades but these are not very fast and should be developed. Azoles AG, AR, AZ, CB, and GL are particularly fast to light.

Azole 6GL is soluble in hot water without any addition, but the others are brought into solution by means of the quantity of hydrochloric acid shown in Table XLIII and 100 times their weight of boiling water. They may be mixed indiscriminately in the dye bath.

The developers recommended are phenol, resorcinol, *B*-naphthol and Azole Developer ON. The colors developed with phenol are too sensitive to alkalies to be of practical value, but when the phenol is combined with other developers, useful shades are obtained. The shades developed with *B*-naphthol are not as fast to light as those obtained with resorcinol or Azole Developer ON. The Azoles have no affinity for cotton or the regenerated rayons and are therefore useful in unions where it is desired to leave the cotton white, or dye it in contrasting shades with direct cotton dyes. Table XLIV gives a list of the colors obtained direct and with various developers.

TABLE XLIII

AMOUNT OF HYDROCHLORIC ACID REQUIRED TO DISSOLVE THE AZOLES

| Each 100 parts of Azole | Requires Hydrochloric Acid |
|---|---|
| AG | 116 Parts |
| AR | 116 Parts |
| AZ | 174 Parts |
| B | 87 Parts |
| D | 87 Parts |
| R | 87 Parts |
| T | 87 Parts |
| CB | 58 Parts |

*Method No. 66: The Azoles on Acetate Silk.* The scoured goods are usually dyed at 55 to 65° C. (130 to 150° F.) in a 30 or 50 to 1 slightly acid dye bath for about an hour. For light shades or to aid leveling, 0.2 to 0.5 per cent of hydrochloric acid, on the weight of the goods, may be added to the dye bath, before sieving in the acid Azole solution. In applying heavy shades 3 to 5 per cent, on the weight of the goods, of sodium acetate crystals, in solution, may be added to the dye bath about a half-hour after entering the goods, to aid the exhaustion. They are then dyed for another half hour and rinsed.

*Method No. 66-A: Diazotizing the Azoles.* The dyed goods may be diazotized in a 20 or 30 to 1 bath with 3 to 6 per cent of sodium nitrite and 7 to 20 per cent of hydrochloric acid. They are rinsed cold and developed immediately.

Phenol, resorcinol and *B*-naphthol are dissolved as described for the Azonines. Azole Developer ON, which is probably *B*-hydroxynaphthoic acid, is dissolved in 2 parts of sodium acetate crystals and 20 to 30 parts of water. The Developers may be mixed in the same bath as desired.

*Method No. 66-B: Developing the Azoles.* Develop the diazotized material for a half to three-quarters of an hour at 45 to 60° C. (115 to 140° F.) in a 20 or 30 to 1 dye bath containing 2 to 6 per cent of developer, on the weight of the goods. Azoles B, CB, D, and T require more developer, in proportion, than the other Azoles. After developing, rinse, soap, rinse, acidulate with acetic or tartaric acid, hydroextract and dry at from 49 to 60° C. (120 to 140° F.). Basic dyes may be used for topping if desired.

TABLE XLIV

COLORS OBTAINED WITH THE AZOLES DIRECT AND DEVELOPED

*Per Cent Azole*

| Developer | 1% AG | 2% AR | 1% AZ | 5% 6GL | 0.75% CB | 5% R | 0.75% B | 0.75% T | 0.5% D |
|---|---|---|---|---|---|---|---|---|---|
| Direct, not Developed | (1) Lemon Yellow | (6) Lighter than 1 | (11) Yellowish-Orange near 2 | | | | | | |
| Phenol | (2) Orange Yellow | (7) Yellow | (12) Browner than 8 | (16) Pale Orange | (20) Near 1 | (24) Lighter than 2 | (28) Near 7 | (32) Pale Orange | (36) Darker than 32, Near 11 |
| Resorcinol | (3) Reddish Orange | (8) Brownish Orange | (13) Dark Reddish Brown | (17) Darker than 16 | (21) Redder than 17 | (25) Darker than 9 | (29) Lighter than 13 | (33) Darker than 13 | (37) Darker than 33 |
| *B*-Naphthol | (4) Lighter and Brighter than 3 | (9) Light Cerese | (14) Dark Bluish Violet | (18) Darker than 17 | (22) Near 21 | (26) Near 3 and 4 | (30) Redder than 10 | (34) Near 10 | (38) Lighter than 14 |
| Azole Developer ON | (5) Bright Cerese | (10) Scarlet | (15) Dark Blue | (19) Reddish Orange Near 3 | (23) Lighter than 5 | (27) Near 5 | (31) Near 15 | (35) Lighter than 15 | (39) Greener and Lighter than 35 |

1.5% Azole AZ diazotized and developed with 4% phenol and 1.5% Azole Developer ON gives a fine dark brown
0.2% Azole T diazotized and developed with 2% Developer ON gives a fine violet
4% Azole D diazotized and developed with 4% Developed ON gives a fine bluish black
4% Azole D diazotized and developed with 3.5% Developer ON and 1% phenol gives a fine black

### *The Silkons*

The Silkons of the Griesheim Elektron Company are another small group of products belonging to this class. It has been stated that Silkon B corresponds to Acedronole AB, while Silkons C and D correspond to Acedronoles CA and DA, respectively. Silkons B and T give direct shades without development, the former a bright yellow (2 per cent) and the latter a more lemon yellow (also 2 per cent). Undoubtedly they are organic bases such as aminoazobenzene, aminoazotoluene, etc. Silkon Developer BON is probably *B*-hydroxynaphthoic acid.

When 2 per cent of Silkon B is diazotized and developed with 2 per cent of Silkon Developer BON, a bright scarlet is obtained, while Silkon T gives an even darker shade under the same conditions. One-half of one per cent of Silkon D with 1.5 per cent of Silkon Developer BON gives a brilliant violet-blue; and 3 per cent of the same Silkon with 1 per cent of Chrysoidine, when diazotized and developed with 4 per cent of this developer, gives a good black. Two per cent of Silkon T, diazotized and developed with 2 per cent of resorcinol, gives an orange-red, while Silkon B gives a deeper red shade under the same conditions. With phenol, Silkon T gives a bright yellow similar to that obtained from Silkon B with the same developer.

*Method No. 67: The Silkons on Acetate Silk.* The Silkons should be dissolved in boiling water with the assistance of hydrochloric acid, as given in Table XLV and then filtered into the dye bath. The goods should be dyed for from three-quarters to one hour at 60 to 70° C. (140 to 158° F.). When dyeing light shades, 0.1 to 0.4 per cent of hydrochloric acid in the dye bath aids in leveling. Rinse once in cold water.

TABLE XLV

AMOUNT OF HYDROCHLORIC ACID REQUIRED TO DISSOLVE THE SILKONS

| Each Pound of Silkon | Require Hydrochloric Acid |
|---|---|
| B | 0.9 Pound |
| D | 0.7 Pound |
| T | 0.8 Pound |

*Method No. 67-A: Diazotizing the Silkons.* Diazotize cold for 20 minutes in a bath containing 1 to 4 per cent of sodium nitrite and 3 to 10 per cent of 32° Tw. hydrochloric acid according to the depth of shade. Rinse once, cold, and develop.

*Method No. 67-B: Developing the Silkons.* Develop for 30 minutes with 1 to 4 per cent of the desired developer, rinse and brighten the shades in a bath containing 1 to 3 per cent of formic acid, on the weight of the goods.

### *Cellit Fast Yellow 2GN*

Cellit Fast Yellow 2GN of the Bayer Company gives a pure yellow directly when applied by Method No. 68 which may be diazotized and developed according to Methods No. 68-A and No. 68-B, to give shades ranging from orange to deep purple or violet. From 1.5 to 2.5 per cent of special Developers A, B, F, H, J, N, or Z are used, according to the color and depth of shade required. When the dyed acetate silk is to be cross dyed on half wool, Developers A, B, F, H, N, or Z are recommended; and for wool, Developers B, F, H, N, or Z. Developer J becomes lighter on wool. Table XLVI gives the colors obtained with 2.5 per cent of the various developers on a 1 per cent dyeing of Cellit Fast Yellow 2GN.

TABLE XLVI
COLORS OBTAINED BY DIAZOTIZING AND DEVELOPING CELLIT FAST YELLOW 2GN

| | |
|---|---|
| Direct without development | Pure Yellow |
| Developer A | Scarlet |
| Developer B | Bluish violet |
| Developer F | Browner-Scarlet than A |
| Developer H | Reddish-Violet |
| Developer J | Orange-Yellow |
| Developer N | Bluer than H |
| Developer Z | Yellowish-Orange |

*Method No. 68: Cellit Fast Yellow 2GN on Acetate Silk.* Use a 30 to 1 dye bath containing 5 per cent of 30 per cent acetic acid and 20 to 30 per cent of sodium sulfate. Dye at 77° C. (170° F.) and rinse.

*Method No. 68-A: Diazotizing Cellit Fast Yellow 2GN.* Diazotize with 3 or 4 per cent of sodium nitrite and 6 or 8 per cent of 32° Tw. hydrochloric acid.

*Method No. 68-B: Developing Cellit Fast Yellow 2GN.* Develop for 30 minutes at 40 to 46° C. (105 to 115° F.) with the desired developers in suitable quantity. Most of the developers are soluble in water but in the case of Developer B, add hydrochloric acid, drop by drop, until the milky color of the solution disappears. Developer N is dissolved by boiling with 60 times its weight of water containing twice as much sodium acetate as developer.

In the case of half-wool unions, the fibers other than acetate silk should be dyed in a neutral Glauber's salt dye bath. Wool is dyed in the usual manner with neutral or acid dyes at a temperature below 80° C. (176° F.).

### *The S.R.A. Diazo Solamines*

The S.R.A. Diazo Solamines of the British Celanese Company were among the first dispersol dyes to be offered for acetate silk. These Diazo Solamines were products suitable for diazotization and development on the fiber, but were applied by the dispersol method of dyeing which will be considered in Chapter XXI. With the advent of the S.R.A. dyes of the same company, which give a wide range of very fast colors directly without development, the Diazo Solamines were withdrawn from the market. Undoubtedly the present S.R.A. Blacks, which are diazotized and developed on the fiber, belong to the class of compounds now under discussion, but as they are applied by dispersol methods, they will be considered with the other S.R.A. dyes.

TABLE XLVII

A COMPARISON OF THE VARIOUS METHODS OF DIAZOTIZATION RECOMMENDED FOR THE DIFFERENT PRODUCTS ON ACETATE SILK

| *Brand* | *Volume of Bath* | *% Nitrite* | *% HCL* | *Temp. °C.* | *Temp. °F.* | *Time* |
|---|---|---|---|---|---|---|
| Acedronoles | — | 2 to 4 | 5 to 10 | cold | cold | — |
| Acetylines | 30 to 1 | 2 to 5 | 5 to 10 | below 15 | below 59 | 20 min. |
| Azoniles | 20 to 1 | 2 to 5 | 4 to 10 | cold | cold | 30 min. |
| Azonines | — | 2 to 4 | 5 to 10 | cold | cold | 20 min. |
| Azoles | 25 to 1 | 3 to 6 | 7 to 20 | cold | cold | — |
| Silkons | — | 1 to 4 | 3 to 10 | cold | cold | 20 min. |
| Cellit | — | 3 to 4 | 6 to 8 | — | — | — |

TABLE XLVIII

A COMPARISON OF THE VARIOUS METHODS OF DEVELOPING THE AZO COLORS ON ACETATE SILK

| *Brand* | *Volume of Bath* | *Temp. °C.* | *Temp. °F.* | *Time* |
|---|---|---|---|---|
| Acedronoles | —— | cold | cold | 30 min. |
| Developer BON | —— | 60 to 70 | 140 to 158 | 30 min. |
| Acetylines | 30 to 1 | 15 to 50 | 59 to 122 | 45 min. |
| Azoniles | 20 to 1 | cold to 49 | cold to 120 | 45 min. |
| Azonines | —— | 45 to 60 | 115 to 140 | 30 min. |
| Azoles | 25 to 1 | 45 to 60 | 115 to 140 | 45 min. |
| Silkons | —— | —— | —— | 30 min. |
| Cellit | —— | 40 to 46 | 105 to 115 | 30 min. |

# CHAPTER XVIII

## *Swelling Agents or Solvents in Dyeing Acetate Silk*

WITHOUT doubt all of these solvent methods of dyeing acetate silk are now obsolete, but they are of interest in showing some of the early difficulties and work in connection with the dyeing of this fiber. Very probably they are the fore-runners of many of our present-day methods. Possibly the use of dyeing "assistants" is based upon these methods, and in fact it is difficult to determine to which class some of the patents belong except from the amount of adjunct material used. It is interesting to note that the use of the various amines and phenols in dyeing acetate silk was first mentioned in this connection,[a] and that soap is also mentioned in connection with the solvents in the same patent.

One of the first patented methods for dyeing acetate silk appears to be German Patent No. 193,135, July 5, 1905, to the Aktien Gesellschaft fur Anilin-Fabrikation. This process is also covered by British Patent No. 1931, January 25, 1906, to C. D. Abel, which states that acetate silk, which cannot be dyed in either an aqueous or alcoholic solution of Methylene Blue, may be dyed in a bath containing both of these solvents. Undoubtedly the acetate silk referred to in this patent consisted of the early primary type of cellulose acetate.

For example, he states that 10 parts of acetate silk may be dyed in about 15 minutes in a bath containing 2 parts of Methylene Blue dissolved in a mixture of 200 parts of water and 150 parts of alcohol. Further examples cover the use of Magenta, Naphthol Yellow S, Erika B, Ponceau 4GB, and Chrysoidine, in amounts varying from 20 to 50 per cent on the weight of the fiber. Methanol, acetone, acetic acid or other suitable solvents that are miscible with water, and in which the dye is soluble, may be substituted for the ethyl alcohol. Aniline in aqueous solution is also mentioned, and dyes of the basic, anthracene, and vat classes are suggested for use by this method.

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[a]United States Patent No. 961,241 and related patents.

French Patent No. 362,721, January 26, 1906, to the same inventor appears to cover a similar process. This proposes to pass the material through a bath containing the dye, organic solvent and water. For instance, 0.2 parts of Fuchsine is dissolved in 50 parts of water and 50 parts of acetone. About 2 parts of acetate silk are worked in this bath for one-half to one hour, after which it is washed. One part of Naphthol Yellow S in 50 parts of water and 50 parts of alcohol may be used, working the acetate silk for one hour at 70° C. (158° F.).

French Patent No. 383,636, November 6, 1907; German Patent No. 199,559, February 19, 1907; British Patent No. 24,284, November 2, 1907; and United States Patent No. 961,241, June 14, 1910, to Knoll and Company, cover the use of organic solvents in dyeing acetate silk. They state that if the fiber is soaked for some time in solutions of the various organic substances, such as 50 per cent aqueous alcohol, or dilute acetic acid, at ordinary temperatures, the fiber swells and after hydroextracting, it may be dyed in the ordinary manner. They suggested the anthracene dyes as well as the basics and mention the fiber's affinity for various amines and phenols or their derivatives. These patents give a good description of the development of the azo colors on the acetate silk fiber, which is discussed in Chapters XVI and XVII, and also mention the use of glacial acetic acid, alcohols, ether, soap, etc., as solvents.

In an addition to the above French Patent (No. 383,636), dated April 5, 1909, the use of inorganic acids, such as hydrochloric acid, in place of the organic substances or their solutions, as mentioned in the principal patent, for treating the acetate silk prior to or during the dyeing, is covered. The inventors state that this acid treatment has the effect of swelling the fiber and increasing its elasticity without any appreciable hydrolytic dissociation. However this latter statement is rather doubtful, as cellulose acetate is hydrolyzed in an acid solution rather rapidly. British Patent No. 7743, March 31, 1909, covers this addition to the original patent.

United States Patent No. 981,574, January 10, 1911, to E. Knoevenagel covers the use of hydrochloric acid in the dyeing of acetate silk, and also mentions hydrobromic, nitric, and sulfuric acids for the same purpose.

The dyeing of fibers and other forms of the fatty acid esters of cellulose, such as cellulose acetate, was covered by the Furst Guido Donnersmarch'sche Kunstseiden-u. Acetatwerke in German Patent No. 228,867, March 15, 1907. They state that the water-repellant nature of the esters may be overcome by the addition of acetin or other organic acid esters of glycerol, glycol, or their derivatives or homologues, to the dye bath. In this case, the shade varies with the quantity of the solvent preparation added. In the same manner, if the solvent preparation is added to the cellulose ester during the process of manufacture, before spinning in the usual manner, the resulting products may be dyed with aqueous solutions of dyestuffs in the usual manner. Also see United States Patent No. 1,532,427, which covers a somewhat similar but later process; and British Patent No. 244,143 on printing dispersol dyes.

Knoevenagel[1] states that while cellulose triacetate is insoluble in water and only very slightly soluble in most organic liquids, it swells in many mixtures of organic liquids and in aqueous solutions of organic and some inorganic substances. These swollen acetates absorb dyes with a speed roughly proportional to the degree of swelling, and the amount of absorption which would require months with the original acetate, is effected in a few minutes with the swollen product. Not only dyes are absorbed by the swollen acetate, but also other organic and even inorganic substances.

A factor which appears to have been overlooked in connection with these products is that according to some of these so-called solvent dyeing methods, it is possible to produce a partial surface hydrolysis of the primary cellulose acetate constituting the older acetates silks, to the later secondary acetone soluble variety, similar to that covered by the Miles patent. This applies particularly to the processes using mineral acids, previous to or during the dyeing, although the same result might be obtained to a smaller extent in aqueous solutions of acetic acid or acetone and especially alcohol or aniline. As these patents were all issued after Miles had applied for his patent, at least some of the inventors may not have overlooked this point.

*Reference*

[1] E. Knoevenagel, *Z. angew. Chem. 24,* 504-5 (1911).

# CHAPTER XIX

## DYEING ACETATE SILK BY SAPONIFICATION

*The Saponification Process and Patents, and Methods of Dyeing the Saponified Acetate Silk*

ONE of the first special methods for dyeing acetate silk was by the saponification, hydrolysis, or deacetylation process, wherein the cellulose acetate composing the fiber was treated with an alkaline solution, usually containing sodium hydroxide, sufficiently strong to saponify a certain portion of the cellulose acetate with a consequent replacement of some acetate radicles with hydroxyl groups, leaving a partially regenerated cellulose or hydrocellulose, somewhat resembling a nitro silk. This method was possibly suggested by the denitration of nitrocellulose in the manufacture of the present nitro rayon, as well as by the Miles patent on the preparation of cellulose acetate, as mentioned in Chapter XVIII.

While the saponification process of dyeing acetate silk was never very successful nor widely used, it is of considerable interest in pointing out what may happen in case the acetate silk is not handled with extreme care in all alkaline solutions, such as in scouring, wetting-out, or dyeing. Very probably the process is not used at all at the present time, except in printing, and therefore the various patents will be considered rather briefly.[1]

There were and still are a number of very serious objections to this method of dyeing acetate silk, yet almost every dyer, in first attempting to dye acetate silk, "discovers" this process during his early experiments and frequently spends considerable valuable time in trying to develop it. One of the principal objections to this method is the difficulty in obtaining level shades on a practical scale. Also the acetate silk loses in weight, as well as some of its most valuable properties, such as luster, strength, water resistance, etc., the amount of this loss depending upon the extent of the saponification.

In this process the amount or depth of the regeneration or saponification depends upon the variety of alkali used in the solution, the strength and temperature of the bath, and the length of time for which it is allowed to act on the fiber. This regenerated cellulose has dyeing properties resembling those of cotton or the other regenerated rayons, and it can therefore be dyed with direct cotton, sulfur, vat or basic dyes, either directly or with mordants, in the usual manner. Many variations and combinations of the saponification and dyeing processes are possible and were used, with more or less lack of success. For instance, in applying certain dyes, the dyestuff itself may be placed in the saponifying bath, the dyeing and saponification proceeding concurrently. Salt may also be added to the alkali bath containing the dyestuff, to aid exhaustion, etc.

A complete saponification of the cellulose acetate constituting acetate silk, with the resulting removal of all acetate groups, would very possibly yield a product with properties somewhat resembling a very inferior grade of ordinary nitro silk. Very probably it would not be as good in many ways as a properly prepared nitro or viscose silk, but we may expect it to dye in a similar manner, and the acetate silk would have lost all of its most valuable characteristic properties. On the other hand, a partial saponification may alter the properties, including the dyeing properties, of the acetate silk only to a limited extent, depending upon the extent of the saponification.

Theoretically, a partial saponification can take place in three ways: (1) The alkali can penetrate and then saponify, the result being a general and uniform lowering of the acetyl value of the total esters; or (2) it may saponify immediately as it comes into contact with the surface of the fiber, before it penetrates into the interior. This of course results in a superficial coating of hydrated cellulose, graduating up to unmodified cellulose acetate in the interior. This result is obtained either by using a dilute caustic alkali solution at a high temperature, or by means of a stronger solution at a lower temperature. The other modification (3) is to use a certain definite quantity of caustic and allow it to act to complete exhaustion. In this manner a certain definite amount of

saponification is obtained and no more. Possibly 2 or 3 give the best results in practice.

However, Haller and Ruperti[2] report that attempts to prepare a partially hydrolyzed acetate silk of low acetate content, by varying the conditions of hydrolysis, failed, the "partially hydrolyzed" products being fully hydrolyzed on the surface but unchanged at the core. They give photomicrographs to illustrate the swelling, optical, and dyeing properties of ordinary and hydrolyzed Celanese.

In the saponification process, the reaction is most rapid during the first five minutes or so after the fiber is entered into the saponifying bath. This rapid action of course results in a rather sensitive process. The original unsaponified fiber has a certain amount of water resistance, which the saponified portion of it no longer possesses to the same extent. For this reason that portion of the fiber first attacked by the alkali rapidly absorbs more water containing alkali and is of course further hydrolyzed, with a resulting very uneven effect.

The literature upon the hydrolysis or saponification of acetate silk has sometimes suggested that the acid and alkaline hydrolysis of acetate silk are similar but Mr. Mork[a] points out where this is in error and shows that there is a very positive difference between these two types of hydrolysis. For example, if Lustron is hydrolyzed with a moderately weak solution of a mineral acid, such as nitric or hydrochloric acid, a gradually increasing affinity for the basic dyestuffs results without destroying the resistance of the fiber to direct dyestuffs until the hydrolysis has progressed to a very marked extent. On the other hand, a mild alkaline hydrolysis will give the Lustron an affinity for direct dyestuffs, before hydrolysis has progressed very far, and the elimination of only 10 per cent of the combined acetic acid will make the yarn dye faster than mercerized cotton with direct dyes. This indicates that at least in some instances the hydrolysis must proceed throughout the fiber and not entirely superficially. Also, Celanese, containing, say, 53 to 55 per cent of combined acetic acid, will not dye with direct dyes, while Lustron hydrolyzed by alkali to the same acid content is readily dyed by the direct dyestuffs.

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[a]Private communication.

*Analysis of Saponified Acetate Silk*

As would be expected, the properties of the partially hydrolyzed acetate silk varies considerably with the extent of the saponification. The extent of the hydrolysis may be determined by analysis, in which the partially saponified fiber is repeatedly extracted with dry boiling acetone in a Soxhlet or other suitable continuous extraction apparatus. This solvent removes only the unsaponified secondary cellulose acetate. In case the fiber contains primary cellulose acetate, which is unlikely in the present products, it should be extracted with chloroform instead of acetone, but in the same manner, and then extracted with acetone, as above. The insoluble residue consists of regenerated cellulose and acetate so altered as to be insoluble in the acetone. The analysis may be carried further by extracting this residue 3 times for 2 minutes each with ten times its weight of cuprammonium reagent, which entirely removes the saponified cellulose, leaving only the partially saponified cellulose acetate. The cuprammonium extract may be acidified and the precipitate washed, dried and weighed.

While the saponification method of dyeing acetate silk was at one time rather widely advocated and numerous patents were granted upon various modifications and combinations of the process, it is not used at present in dyeing acetate silk and is no longer recommended. A very good reason for this is that with the many new and excellent dyes for this fiber now available, this always more or less unsatisfactory process is no longer needed. The saponification process which was formerly recommended by several companies is given in Method No. 69. While the original patent upon the saponification process for dyeing acetate silk was issued to Mr. H. S. Mork, of the Lustron Company, this particular method is covered by British Patent No. 169,741, April 29, 1920, to the British Cellulose and Chemical Manufacturing Company, and United States Patent No. 1,425,364, August 8, 1922, to Briggs, assigned to the American Cellulose and Chemical Company.

*Method No. 69: Saponifying Acetate Silk.* Thoroughly scour the acetate silk as in Method No. 5 and enter 10 pounds of it into a 100 gallon bath containing 3 pounds of 72° Tw. sodium hydroxide solution heated to 75° C. (167° F.). Hold the bath at this tem-

perature and work the goods for 45 minutes. Wash the material in warm water until free of alkali and sour in a dilute acetic acid solution. Rinse again, wash in soft water, and soap lightly. Where the goods are to be dyed immediately, the souring and subsequent operations may be omitted.

This particular method is stated in the patent to apply especially to acetate silk containing 2 to 2.5 acetate groups per cellulose molecule, and temperatures of from 40 to 80° C. (104 to 176° F.) are mentioned as suitable. The quantity of alkali is restricted to that necessary to produce not more than a 10 per cent loss in weight in the acetate silk originally present. The above formula gives about this loss in weight. Sodium hydroxide or carbonate, or potassium hydroxide in not over one per cent concentration are mentioned as suitable alkalies. A provisional specification covers the saponification of any acetate lower than cellulose triacetate and states that the restricted saponification may also be affected by using an excess of reagent for only a limited time of action. It also refers to British Patent No. 158,340, covering the use of ammonium thiocyanate.

The best result which the author has seen along this line was obtained by the use of Mordant LB of the Liberty By-Products Company. Mr. Ernest A. F. Zillessen, working under Mr. Mork's basic patents upon the saponification process of dyeing, developed this product, which consists of a special mixture of sodium carbonate and a colloid. Zillessen found that on saponifying acetate silk by the usual process, *i.e.*, in a bath containing about 10 grams of soda ash per liter at 85° C. (185° F.) for an hour, the addition of, say, 5 grams per liter of a suitable colloid, such as gelatin, casein, or glucose, to the bath, gave a much more level saponification with a minimum loss in weight by the fiber. In this way he is able to saponify Celanese sufficiently to apply the direct cotton dyes, as for instance Noil's Direct Fast Scarlet B, in medium shades, with only a 3 per cent loss in weight of the acetate silk and only a very slight reduction in luster. While the process appears to work very nicely on acetate silk effects, where solid colors are desired, it has not proven satisfactory on all Celanese piece goods, etc. Neither has it been used very extensively in skein dye-

ing, due to the loss in weight of the fiber. However, in many cases where the fastness of the direct colors are satisfactory, it is cheaper than the use of some of the special acetate silk dyestuffs.

*Saponification Process Patents*

As mentioned before, the first patented saponification process for dyeing acetate silk appears to be that covered by United States Patent No. 1,061,771 (1913); French Patent No. 416,752, June 4, 1910; and British Patent No. 20,672, September 5, 1910, to H. S. Mork of the Lustron Company.

Cross and Dreyfus, in British Patent No. 125,153, June 19, 1916, suggested the use of an ethyl or methyl alcoholic medium with a fractional equivalent of alkali or base so that the alcohol of the medium takes part in the subsequent saponification of the acetate.

British Patent No. 150,989, May 17, 1920; and United States Patent No. 1,366,023, January 18, 1921, to the Société Chimique des Usines du Rhone, anciennement Gillard, P. Monnet, et Cartier, covers the use of hot or cold solutions of metallic salts, to which alkali has been added, and mentions sodium chloride and hydroxide.

British Patent No. 183,806, May 17, 1922, and United States Patent No. 1,440,501, January 2, 1923, to the same society, covers the partial saponification of acetate silk by means of trisodium phosphate, prior to or during dyeing. Swiss Patent No. 100,708 to the Société pour la Fabrication de la Soie "Rhodiaseta" appears to cover the same process.

British Patent No. 192,994, April 19, 1922, an addition to the above Patent No. 150,989 to the same inventors, covers the use of a neutral salt of an alkali metal, to which has been added, in the place of the alkali, as in the principal patent, a salt having an alkaline reaction and adapted to effect the desired saponification. For example: 100 grams of acetate silk may be soaked in a 2 liter bath containing 800 grams of sodium sulfate and 15 grams of trisodium phosphate for about 1 hour at 70 to 80° C. (158 to 176° F.), or until the solution fails to react alkaline. It is then washed and dyed. Sodium borate, silicate, and carbonate are also mentioned.

Richardson in United States Patent No. 1,442,631, January 16, 1923, and British Patent No. 176,034 of 1920, covered the use of sodium acetate in alkaline saponifying baths. British Patent No. 175,486 of 1920 to the British Celanese Company covers the use of alkali silicates, aluminates, and borates in saponifying baths, the aim being to secure a more level effect.

British Patent No. 193,912 and No. 194,244, November 2, 1921, to W. Bader and the British Cellulose and Chemical Manufacturing Company cover the partial saponification of acetate silk with a 2 to 15 per cent solution of caustic soda, controlling the saponifying action by means of low temperatures; by adding alkali metal salts; or by the precipitation of insoluble soap films on the fiber. For example, the acetate silk may be saturated with a solution of soap and afterwards treated with brine, whereby the fibers become coated with a protective film of soap. They are then treated with a 10 per cent solution of caustic soda for 15 to 20 minutes. Or the acetate silk may be first treated with concentrated solutions of such salts as the chlorides of sodium, calcium, or magnesium, after which the saponification is claimed to be more regular. Small amounts of alkali or alkali-earth hydroxides may be added to the saline solution. This preliminary treatment has a specific action on the acetate silk, so that the superficial saponification effect can be obtained even when the salts employed have been completely washed out of the fiber. For example, acetate silk is soaked for 2 hours in a 25 per cent solution of sodium chloride, or boiled for 10 minutes in the solution. It is then saponified in a cold 5 per cent solution of sodium hydroxide. It is claimed that the dyeing properties are greatly improved, while the loss in weight is only 1 or 2 per cent.

In British Patent No. 195,920, November 2, 1921, to Bader and the British Cellulose and Chemical Company, the partial saponification of acetate silk is effected in a cold one per cent caustic alkali solution, the action of which is accelerated by the presence of finely divided solids, either suspended in the saponifying bath or precipitated on the fiber. Clay, alumina or silicic acid gel, prepared so as to be insoluble in cold dilute alkali, may be added to the caustic solution, or the fiber may be treated in such a manner as to form

insoluble precipitates on it, such as calcium carbonate, magnesium oxide or carbonate, aluminum, or calcium oleate, etc. In a modification, alkali aluminates are dissolved in the saponifying liquid and these deposit a colloidal hydrosol on the fiber. For example: acetate silk may be soaked for 2 hours in a 25 per cent solution of sodium chloride, then squeezed and suspended in a 40 to 1 solution containing 30 per cent of aluminum sulfate, on the weight of the fiber, sufficient caustic soda to convert it into sodium aluminate ($NaAlO_2$), and excess of caustic soda equal to 10 per cent of the weight of the acetate silk. Saponification is complete in about 2 hours.

According to British Patent No. 209,849, October 21, 1922, to the Badische Company, the alkaline saponification of acetate silk may take place in the presence of soluble aldehydes or hydroxy aldehydes, or their salts, or mixtures of the above aldehydes and acids. The process may be varied to give the fiber either an increased or decreased affinity for dyes. French Patent No. 558,900 covers a similar process, in which it is claimed that neither the strength or luster of the acetate silk is impaired. The treatment may take place prior to or during the dyeing process.

A recent French process of saponifying acetate silk is covered by French Patent No. 590,738, February 15, 1924, to Teinturerie de la Rize. In this process the fiber is treated for from 15 minutes to 2 hours at 50 to 70° C. (122 to 158° F.) with an aqueous solution containing 1 kilogram each of barium hydroxide and barium chloride in each 100 liters of bath.

United States Patent No. 1,489,814, April 8, 1924, to M. E. Bouvier covers the treatment of acetate silk in a concentrated solution of neutral alkaline salts, containing not more than one per cent of an alkali salt capable of hydrolyzing the fiber. For example: Water 2 liters, sodium sulfate 350 grams, and sodium carbonate 17 grams.

### *Dyeing Saponified Acetate Silk*

The dyeing of saponified acetate silk proceeds in exactly the same manner as the dyeing of viscose rayon, except that temperatures below 75° C. (167° F.) should be used. The direct cot-

ton, as well as the other dyes generally used on viscose, are very satisfactory for this purpose. When the sulfur dyes are to be used, they are generally applied in a combined saponifying and dyeing operation, using a strongly alkaline bath containing the alkali, sulfide, and dyestuff. Many other dyes may be applied concurrently also, particularly the vat dyes. However this combined saponifying and dyeing process is subject to the same criticisms as applied to the other saponification processes of dyeing.

A combined saponification and dyeing process is covered by British Patent No. 178,946, January 27, 1921, to Briggs, Richardson, and the British Cellulose and Chemical Manufacturing Company. This process is given in Method No. 70. British Patent No. 224,218, November 3, 1923, to the Société Alsacienne de Produits Chemiques covers another combined process. In this patent it is suggested to use a saponifying and mordanting bath containing sodium hydroxide or phosphate with a sulfurized compound of phenol[b] (Katanol) or its derivatives or substitution products. It is stated that the shades obtained with basic dyes are similar to those obtained on a tannin mordant and that the treatment with antimony salts is not necessary. The mordant may be used in the same bath with substantive or sulfur dyes. when these are to be topped with basics.

*Method No. 70: Combined Saponification and Dyeing of Acetate Silk-Cotton Unions.* The union is worked in a dye bath containing small quantities of soap and/or soda ash at a temperature below 50° C. (122° F.) until the cotton is fully dyed, leaving the acetate silk slightly stained. The temperature of the bath is then raised to 75 or 80° C. (167 or 176° F.) and a small amount of alkali, that is up to 10 per cent of sodium hydroxide, on the weight of the acetate silk, is added. As the saponification proceeds, the color bleeds from the cotton onto the acetate silk. It is claimed that by properly controlling the process, level shades may be obtained. Sodium carbonate, sulfide, silicate, aluminate, and borate, as well as the hydroxide, are suggested as saponifying agents.

The following dyes have been particularly recommended for

[b]See British Patent No. 215,012.

the saponified acetate silk. Those starred have exceptional fastness to light. Chlorazol Fast Yellow B and Chlorazol Fast Red FG9202K are direct dyes which are not decomposed by sodium sulfide and may therefore be used in the same bath with sulfur dyes for shading.

| | |
|---|---|
| Chlorazol Fast Yellow NX | Chlorazol Fast Red FG9202K |
| Chlorazol Fast Orange D | Thionol Corinth RBX |
| *Chlorazol Fast Red K | *Thionol Blue 2B |
| Chlorazol Violet N | Thionol Black Brown B9146K |
| *Chlorazol Fast Blue 2B | Thionol Black XXN conc. |
| Chlorazol Sky Blue GW | *Thionol Black OG |
| *Chlorazol Green BN | *Cross Dye Sky Blue FFS |
| Chlorazol Dark Green PL | *Cross Dye Green 2G Concentrated |
| *Chlorazol Brown M | Cross Dye Brown 2R |
| Chlorazol Black E extra | *Cross Dye Black BX |
| Chlorazol Black BH | Cross Dye Yellow Y |
| *Chlorazol Fast Yellow B | |

While the saponification process of dyeing acetate silk has been almost entirely superseded[3] by the use of the many special dyes for acetate silk, it is still used in a few cases for printing, etc. At best, the process is extremely difficult to control on a large scale and on all classes of goods. In every case the fiber loses weight, and if the saponification is carried very far, it also shrinks, loses luster, strength, water resistance, and of course cross-dyeing properties. However, a full understanding of the process is very important to all dyers, as many of their troubles in handling acetate silk may be traced to a partial hydrolysis of the fiber in some previous process, such as scouring.

*References*

[1] C. E. Mullin, *American Dyestuff Reporter 14,* 382 (1925).
[2] R. Haller and A. Ruperti *Leipzig Monato. 40,* 353 and 399 (1925).
[3] B. Roetel, *Textilber 7,* 43-4 (1926).

# CHAPTER XX

## THE IONAMINES

*The Development of the First Special Dyestuffs for Acetate Silk. The Patents Covering Them. Their Application to, and Properties on, Acetate Silk.*

THE fact that many compounds insoluble in water dye acetate silk, and that the usual method of solubilizing dyestuffs, that is by sulfonating, usually destroys the affinity of the product for acetate silk, led to research for a new method of solubilizing the insoluble bases, dyes, etc., without reducing their affinity for the acetate silk. Several methods of solubilizing without introducing the sulfonic group have been mentioned, such as the introduction of the carboxyl and other acidic groups, etc., but the Ionamines are entirely new products, quite different from those mentioned, and are applied by an entirely new method. They were the first products developed to meet the exacting requirements of the acetate silk dyeing industry and are today one of the most important groups of dyes for this purpose.

According to Green and Saunders,[1] various dyeing experiments on acetate silk led to the theory that dyestuffs containing hydroxy alkyl radicles attached to nitrogen might have an affinity for acetate silk by virtue of their alcoholic groups. However, the azo compounds of this type prepared, which included dihydroxyethyldiaminoazobenzene, nitrobenzeneazodihydroxyethylaniline, and benzeneazobisdihydroxypropylaniline, were not highly successful. While the simpler bases which were soluble in water had an affinity for acetate silk, the affinity decreased as the number of alcoholic groups increased, thus disproving the hypothesis.

It was then concluded that the dyeing of acetate silk was mainly a solution problem conditioned by the following factors: (1) The dye should contain amino, substituted amino, or hydroxyl groups; and strong salt forming groups, such as the sulfonic group should be absent, or if present they greatly reduce or obviate the dyeing affinity. (2) When basic compounds are used as their salts with

acids, such as dyestuff-hydrochlorides, the salt should be readily dissociated by water, as it is the base and not the salt which is absorbed by the fiber. (3) The free base should be at least sparingly soluble in water. (4) As high molecular complexity tends to diminish solubility in non-aqueous solvents, such as acetate silk fiber, the molecule should not be too large. By the application of these rules (which in most respects parallel very closely those on which the S.R.A. dispersol dyes were later developed, as well as Clavel's theory), after considerable research, compounds were produced which were more or less soluble in water, and which hydrolyzed in solution as desired, giving the sparingly soluble base of not too complex form to be absorbed by the acetate silk.

The actual products eventually used are the omega-sulfonic acids of amino compounds of the general formula $X.NR'.CHR''.SO_3H$, in which X is a hydrocarbon nucleus, and R′ and R″ are alkyl groups or hydrogen. While such compounds are not new[2] they had not previously been used commercially as dyes.[a] The simpler compounds of this class, which are colorless, are formed by treating primary or secondary amines with aldehyde bisulfites, such as formaldehyde bisulfite, or formaldehyde and sodium bisulfite, as

$$C_6H_5.N{:}N.C_6H_4.NH_2 + HCOH + NaHSO_3 \longrightarrow C_6H_5.N{:}N.C_6H_4.NH.CH_2SO_3Na.$$

Aniline Yellow (Insoluble) Soluble Ionamine

[a]The first patent covering an omega-sulfonic acid compound appears to be British Patent No. 11,343, May 31, 1899, to C. D. Abel for the Actienges. fur Anilinfabrikation. It states that by treating anhydroformaldehyde compounds of aromatic amines having the typical formula $R.N{:}CH_2$ with sulfurous acid or bisulfites, acids are obtained having the typical constitution $R.NH.CH_2SO_3H$, which are well characterized substances, and readily soluble in sodium carbonate solutions and in caustic alkalies. On combining them with suitable diazo compounds, and replacing the $CH_2SO_3H$ group with hydrogen, by treating the azo compounds with alkalies, alkaline carbonates, or mineral acids, mixed amidoazo compounds may be obtained. For example a mixture of 11.9 kilos of anhydroformaldehyde-*o*-toluidine and 60 kilos of 32° Be. sodium bisulfite solution are mixed until it solidifies as a mass of methyl-*o*-toluidine-omega-sulfonic acid. Or, the solution of *p*-nitrodiazobenzene chloride from 6.9 kilos of *p*-nitroaniline is added to a cold solution of 10.5 kilos of sodium methylaniline-omega-sulfonate and 13.6 kilos of sodium sulfate in 50 liters of water . After filtering off the dyestuff, it is mixed to a paste with water and heated with 6 kilos of sodium hydroxide in 200 liters of water. Formaldehyde is given off, and, on acidulating, sulfurous acid is evolved. The reaction is complete after boiling for a half hour, when the dyestuff is filtered off and washed with water.

These omega-sulfonic compounds, while stable in neutral solution, have the desired property of readily hydrolyzing on heating in the presence of dilute acids or alkalies, to give the corresponding amine or amino compound and the aldehyde bisulfite compound or its decomposition products, as follows:

$C_6H_5.N:N.C_6H_4.NH.CH_2SO_3Na + HCL + H_2O \longrightarrow$
$C_6H_5.N:N.C_6H_4.NH_2 + HCOH + SO_2 + NaCl + H_2O$; and,
$C_6H_5.N:N.C_6H_4.NH.CH_2SO_3Na + NaOH + H_2O \longrightarrow$
$C_6H_5.N:N.C_6H_4NH_2 + HCOH + NaSO_3 + H_2O$.

While the base is nearly insoluble in water, it is soluble in acetate silk, and has the usual high affinity of the amino compounds for it. The readily hydrolyzable character of the Ionamines is due to the fact that the sulfonic group is situated externally to the nucleus of the dye proper.

Such azo dyes, depending entirely upon the omega-sulfonic acid groups for solubility, behave in general like acid dyes and the free aminoazo base dyes acetate silk, especially in a slightly acid or alkaline bath. This free base can in most cases be diazotized and coupled with phenols or amines on the fiber, as described in Chapters XVI and XVII. The products derived from primary amino compounds contain free amino groups and may be diazotized and developed, giving a wide range of fast colors. The products derived from secondary amino compounds may be used for direct shades but are not diazotizable. Methyl-omega-sulfonic acid compounds of aminoanthraquinone may be prepared in the same manner as these aminoazo compounds and are applied in the same manner. Probably some of these give direct shades of excellent fastness. These methyl-omega sulfonic acid compounds, while quite different from the sulfato acid dyes of Chapter XIV, which are very stable in acid or alkaline solution, form an interesting comparison with them.

These omega-sulfonic acid products are called Ionamines and are applied in slightly acid or alkaline dye baths at about 65 to 75° C. (140 to 167° F.). They have a good affinity for acetate silk and exhaust well even in dilute baths without the addition of salt. In the presence of sufficient acid they level well, if the temperature of the bath is not increased too rapidly. The dye bath should be

about 20 to 100 times the weight of the material. In dyeing cord or fabrics which require deep penetration, it is best to work the material well in a neutral dye bath and then acidify and warm the bath gradually during the dyeing.

The Ionamines which have the greatest affinity for acetate silk have the least affinity for cotton, and those which have the greatest affinity for cotton have least for acetate silk. The other artificial silks react to the Ionamines in the same manner as cotton. Wool is dyed by the unhydrolyzed dye in an acid bath, but not by the free base after hydrolyzation, as is the acetate silk.

The first Ionamines were divided into two classes: Those containing one salt forming group within the molecule, such as Ionamine B; and those containing two salt forming groups, such as Ionamine A. The later nomenclature adopted for the Ionamines uses distinguishing letters only to denote those intended for developing colors, while the direct dyeing Ionamines are denoted by the color produced. The Ionamines containing only one salt forming group have greater stability to hydrolysis and when dyed are not greatly affected in shade by organic acids. Those containing two salt forming groups are more easily hydrolyzed and may be applied with formic or acetic acid, sodium carbonate, sodium acetate, or in a neutral bath. When dyed, the direct shade is easily affected by dilute organic acids, but when diazotized and developed they are fast and give deep shades.

In diazotizing and developing Ionamines containing two free amino groups, care must be taken to insure complete tetrazotization and coupling or the color will not be fast. Only the unsulfonated phenols are useful in developing and *B*-naphthol, resorcinol, or *B*-hydroxynaphthoic acid are particularly recommended. Sulfonated developers, such as R-salt, do not penetrate the fiber. Various combinations of these with the different Ionamines give a wide range of colors, very fast to washing, light, perspiration, rubbing, etc.

In general, the light fastness of the colors developed with resorcinol is usually better than with any other developer, while those developed with *B*-hydroxynaphthoic acid come next. The objection to basic developers, such as *m*-phenylenediamine, is that they

may be taken up by the fiber in excess and later mark off on white material. This fault may possibly be overcome by using a sufficiently weak bath. Ethyl-*B*-naphthylamine gives violet to blue shades with several Ionamines but these colors are not fast to light. *B*-Hydroxynaphthoic acid is recommended for blue and black shades and it should be noted that when applied from a slightly acid solution, it gives deeper and faster shades, especially to light.

Interesting two-color effects are obtained on cotton-acetate silk unions dyed either in one bath or by cross-dyeing. In dyeing wool-acetate silk unions, it must be remembered that the unhydrolyzed dye acts as an acid dye on the wool and this must be taken into account. Natural silk is partly dyed by the hydrolyzed and partly by the unhydrolyzed dye. All this points to a wider use for the Ionamines than on acetate silk alone, owing to their combined acid and basic properties.

The colors available vary from yellow and orange to scarlet, red, maroon, violet, blue, and black. However there does not yet appear to be any brown or direct black Ionamines. Cellutyl Union Black R is a mixture of a direct cotton black and an Ionamine in such proportions as to give a uniform black on cotton-acetate silk unions upon developing with *B*-hydroxynaphthoic acid. Recently special attention has been paid to the development of new Ionamines containing only one salt forming group, similar to the original Ionamine B, as these dyes are of satisfactory fastness when dyed direct without diazotizing and developing. It was particularly difficult to find a fast blue, as the aminazo, disazo, and induline compounds tried were unsatisfactory. While the omega-sulfonic acid compounds of gallocyanine combined with paradiamine gave reddish-blue to violet shades in neutral baths, they were not fast to light. The Ionamine Blue R and G eventually produced are the omega-sulfonates of unsulfonated aminoanthraquinones[a] and have excellent light fastness. These dye in the same manner as the other members of the group but do not exhaust as completely. The difficulty described under Phototropy[b] was also encountered in developing the Ionamines.

[a] See British Patent No. 211,720.
[b] See Chapter VIII.

In practical dyeing some difficulties were experienced in obtaining through penetration with Ionamines containing a very insoluble base, such as Ionamine A, but this was overcome by entering the material at about 30° C. (86° F.) in a dye bath containing 3 to 5 per cent of mineral acid and increasing the temperature very slowly to about 75° C. (167° F.) and dyeing for about one-half hour or longer. In this manner the hydrolysis of the dye is retarded, allowing it to penetrate the material. As before stated, the Ionamines may be either primary or secondary, according to whether the amino group carrying the alkyl omega-sulfonic acid group is primary or secondary. Usually the secondary Ionamines have better penetrating qualities than the primary, and are therefore more level dyeing. The two groups can readily be differentiated by the action of nitrous acid which decolorizes the secondary Ionamines without forming a coupling diazo compound.

The advantages in using the Ionamines would appear to be their solubility in water, and the fact that they are not precipitated by acids, alkalies, or salt, and under suitable conditions can be applied in the same dye bath with the cotton colors. One of the main difficulties which may arise in their practical application is the matter of obtaining a wide range of dyes that will hydrolyze, within reasonable limits, at approximately the same rate under similar conditions in the dye bath, as regards acidity or alkalinity and temperature. This may become a matter of considerable importance in large scale dyeing of the various innumerable mixtures required for all shades.

It is also stated that under certain conditions of applying the developed Ionamines the silk may lose its luster or go "blind," possibly due to the formation of crystalline compounds on or near the surface of the fiber.[3] In fact it is claimed that such a crystalline formation can be seen with the microscope under certain conditions. Such blindness may also occur with other developed colors on acetate silk and is not confined to the Ionamines alone. In general the Ionamines have a greater affinity for Celanese than for Lustron, and therefore, when applied in the same bath, the Celanese is usually somewhat darker than the Lustron. However, the Ionamines as well as the other developed colors may be used

on Lustron and Rhodiaseta just as well as on Celanese with the same fastness properties. As the actual coloring matter is usually largely produced within the fiber, the dye bath is generally clear throughout the dyeing operation, the color penetrating well and remaining firmly fixed in the fiber.

*Method No. 71: Dyeing Acetate Silk with Ionamine A.* Ionamine A is used mainly for black with *B*-hydroxynaphthoic acid but may also be used as a direct yellow (2 per cent). Its various fastness properties are given in Table XLIX. This dye is not as soluble as most of the Ionamines but the presence of a certain amount of insoluble dye does not interfere with either its leveling or penetrating properties, and it exhausts well from the dye bath. Five per cent of the Ionamine with six per cent of B-hydroxynaphthoic acid gives a good black which is the standard for acetate silk. The acetate silk scoured by Method No. 10, without the souring, is entered into the lukewarm dye bath containing the dye and 2 per cent of soda ash or 1 per cent of formic acid. In one-half hour the temperature of the bath is raised to 75° C. (170° F.) and held there for three-quarters to one hour when the bath should be exhausted. In place of the formic acid, 2 per cent of soda ash, 0.25 per cent of sulfuric or 0.5 per cent of hydrochloric acid may be used in the dye bath, but salt or sodium sulfate are of no advantage. If the shade is not to be developed, the goods may pass through an alkaline bath containing a little ammonia or soda ash.

*Method No. 71-A: Diazotizing the Ionamines.* If the shade is to be diazotized, it is rinsed without neutralizing the acid and diazotized in a bath containing 5 per cent of sodium nitrite and 10 to 15 per cent of 32° Tw. hydrochloric acid for 20 minutes for medium shades.

*Method No. 71-B: Developing the Ionamines.* The diazotized acetate silk is rinsed and entered into a cold developing bath containing 3 to 6 per cent of developer, on the weight of the goods, and the temperature raised to 50 or 60° C. (122 or 140° F.) for about one-half hour. Under-development may occur at lower temperatures. When *B*-hydroxynaphthoic acid is used as the developer, as for black, it should be dissolved by boiling it with one-half

of its weight of sodium carbonate in water, or treating it with sodium hydroxide solution. The *B*-hydroxynaphthoic acid developing bath should contain about 300 parts of water to each part of developer, and before entering the diazotized goods, the bath should be made slightly acid by the addition of about an equal weight of glacial acetic acid, or its equivalent. The condition of the developed acetate silk may be improved by rinsing well and soaping for 20 minutes at 50° C. (122° F.) in a bath containing 2 pounds of soap per 100 gallons of water. When *B*-naphthol is used as the developer, the bath should be slightly alkaline, and is prepared by dissolving the naphthol in a minimum amount of sodium hydroxide solution, which is usually about an equal weight of 76° Tw. solution. This is diluted in the developing bath and used cold.

Ionamine B may be applied in the same manner as Ionamine A, Method No. 71, except that 2 per cent of formic acid should be used. When dyed direct, 5 per cent gives a deep orange color. When this is diazotized and developed with 6 per cent of *B*-napthol, as in Method No. 71-A, a bright scarlet is obtained. Substituting the same quantity of resorcinol or *B*-hydroxynaphthoic acid for the *B*-naphthol gives cerese or crimson-red, respectively.

*Method No. 72: Ionamine H.* Ionamine H is used both as a direct shade for a yellowish green (2 per cent) or with *B*-naphthol for bluish-red. It may also be developed with resorcinol or *B*-hydroxynaphthoic acid. In the latter case a bluish-violet is obtained which is sensitive to both alkalies and acids. It has good penetration. The dye is soluble in hot water and is applied in the same manner as in Method No. 71 for Ionamine A, except that 2 per cent of formic acid is used, or 1 per cent of sodium carbonate may be substituted for the acid. One-half per cent of sulfuric or 1 per cent of hydrochloric acid may also be used in place of the formic acid. It is diazotized and developed in the same manner as in Methods No. 71-A and No. 71-B.

*Method No. 73: Ionamine L paste.* This Ionamine is in the form of a paste and is very soluble in water. It has good penetrating properties and may be used alone as a direct yellow, or with the various developers as shown in Table XLIX. It is applied as in Method No. 71 but with only 1 per cent of formic acid,

and may be finished or developed as in Method No. 71-A and No. 71-B. *B*-Naphthol developer is prepared as in Method No. 71-B or resorcinol is dissolved in hot water only and used in a bath containing 6 per cent of developer. In any of these developing baths, if a standing bath is used, an addition of about 2 per cent of developer is made after each lot of goods has passed through the bath.

Ionamine MA gives a direct yellow on acetate silk which may be developed to orange or red shades with *B*-hydroxynaphthoic

TABLE XLIX
FASTNESS PROPERTIES OF THE IONAMINES

| | | *Ionamine A* | | |
|---|---|---|---|---|
| | *Direct* | *B-hydroxy-naphthoic Acid* | *B-naphthol* | *Resorcinol* |
| Shade | Yellow | Black or Navy Blue | Reddish-purple | Reddish-brown |
| Washing | very good | very good | | |
| Mineral Acids | Poor | very good | | |
| Soda | very good | good | | |
| Perspiration | very good | very good | | |
| Hot Pressing | very good | very good | | |
| Light | poor | fairly good | | |

*Ionamine H*

| *Direct* | *B-Naphthol* | *B-hydroxynaphthoic Acid* | *Resorcinol* |
|---|---|---|---|
| Orange-Yellow | Reddish-Purple | Purple | Reddish-Brown |
| very good | very good | | |
| poor | good | very poor | |
| fair | fair | very poor | |
| very good | very good | | |
| good | good | | |
| good | poor | | |

*Ionamine L*

| *Direct* | *Resorcinol* | *B-Naphthol* | *B-hydroxynaphthoic Acid* |
|---|---|---|---|
| Dull Yellow | Reddish-Brown | Purple | Bright Blue |
| very good | very good | very good | very good |
| poor | good | very good | very good |
| poor | poor | very good | fair |
| very good | very good | very good | very good |
| very good | very good | very good | very good |
| fairly good | good | poor | poor |

*Ionamine B*

| *Direct (5%)* | *Resorcinol* | *B-Naphthol* | *B-hydroxynaphthoic Acid* |
|---|---|---|---|
| Deep Orange | Reddish-orange | Scarlet | Crimson |

acid. Ionamine Red GA gives a terra-cotta red (1 per cent) which may be developed. Ionamine Red KA gives a direct scarlet which may be developed with resorcinol to orange brown; *B*-naphthol to a claret; or with *B*-hydroxynaphthoic acid, to a bordeaux shade. Ionamine Orange CB gives very brilliant direct shades of excellent fastness. The above are generally applied from a dye bath containing 2 per cent of formic acid at about 75 to 80° C. (167 to 176° F.). Ionamine Blue B is the latest addition to the list. It is very fast to light and washing, being equal to the Duranol dyes in this respect. It is a readily soluble powder and should be applied without mineral acids. Table L gives some properties of the direct Ionamines.

All of the Ionamines may be dyed with 1 to 2 per cent of formic acid, and Ionamines MA, B, and H, with sodium carbonate, as in Method No. 71. The Ionamines are used as follows:[4]

For direct dyeing only

Ionamine Red KA
Ionamine Orange CB
Ionamine Blue B

For both direct and developed dyeings

Ionamine MA (yellow)
Ionamine B (orange)
Ionamine GA (red)

For diazotized and developed dyeings only

Ionamine H
Ionamine L paste
Ionamine A

TABLE L
PROPERTIES OF THE DIRECT IONAMINES

| *Name* | *Type* | *Properties* |
|---|---|---|
| Ionamine Yellow MA | Primary | Gives a slightly phototropic golden yellow color which closely resembles that of Ionamine B in all its fastness properties. |
| Ionamine Orange B | Primary | The original Ionamine B |
| Ionamine Orange CB | Secondary | Gives a bright reddish-orange very fast to light, penetrates twist better than B, and is suitable for all classes of work. |
| Ionamine Red GA | Primary | Gives a terra-cotta red color, exhausts well, and is very fast to light. Suitable for all classes of work. |
| Ionamine Red KA | Secondary | Dyes a red and gives a solid shade on unions with Chlorazol Fast Red K, of good fastness to light. |
| Ionamine Blue B | | Gives a sky blue color very fast to light and washing. |

When the Ionamines are used with the direct cotton dyes on acetate silk-cotton unions, it is best to apply them from an alkaline or soda ash bath rather than from an acid bath, and most of the Ionamines may be applied in this manner. The following abstracts give some information as to the general methods of manufacture, the products used in, and the constitution of the Ionamines.

*The Ionamines Patents*

What appears to be the first patent covering the Ionamines is British Patent No. 197,809, April 5, 1922, to A. G. Green, K. H. Saunders, and the British Dyestuffs Corporation, and covers a process of manufacture. United States Patent No. 1,483,798, February 12, 1924, covers the same process. In this patent it states that although compounds having the general formula $X.N_2.Y.NH.CH_2.SO_3H$ are very unstable in alkaline solution, those containing a nitro group in the para-position of the nucleus (X), may be reduced with sodium sulfide to the corresponding diaminoazo compounds, without splitting off the methyl-omega-sulfonic acid radicles.

In the same manner disazo compounds having the general formula $X.N_2.Y.N_2.Z.NH.CH_2.SO_3H$, in which X contains a para-nitro group, may be reduced to the corresponding diaminodisazo compounds. By subsequent treatment of these diaminoazo compounds with sodium bisulfite formaldehyde, a second methyl-omega-sulfonic radicle may be introduced. For example: When 13.8 parts of *p*-nitroaniline are diazotized and coupled with 20.9 parts of sodium methylaniline-omega-sulfonate, on neutralizing the resulting 1300 parts of solution with sodium carbonate and stirring, most of the nitroazo dyestuff will separate as a fine suspension. On adding a cold solution containing 50 parts of sodium sulfide crystals in 200 parts of water, and stirring for 16 hours, complete reduction is effected, and the resulting diaminoazo compound may be salted out, filtered off and used to dye acetate silk from a slightly acid dye bath. It has no affinity for cotton. In the same manner 13.8 parts of diazotized *p*-nitroaniline may be coupled with 25.9 parts of sodium methyl-*a*-naphthylamine-omega-sulfonate ($C_{10}H_7.NH.CH_2.SO_3Na$). The product is reduced with

60 parts of sodium sulfide crystals to give a water-soluble product which dyes acetate silk directly from a slightly acid bath.

British Patent No. 200,873 (1922) and United States Patent No. 1,483,797, February 12, 1924, to Green, Saunders, and British Dyestuffs Corporation, cover the application of the Ionamines. It specifies methyl-omega-sulfonic acids, derived from amino- or monoalkylamino-azo compounds, dissociated slowly in hot aqueous solutions which are slightly acid or alkaline, and the free (colored) amino- or alkylamino-azo bases thereby liberated are readily absorbed from solutions by the acetate silk. The colored bases absorbed by the acetate silk may be diazotized and developed with suitable phenols, amines, or aminophenols, with consequent change of shade. In this manner acetate silk may be dyed many shades except green. Ethyl-omega-sulfonic acid and analogous acids are also mentioned, but they are less stable towards acids and alkalies. In printing the alkyl-omega-sulfonic acid is applied in a thickened paste containing an organic acid, after which it is dried and steamed.

British Patent No. 212,029, January 13, 1923, and United States Patent No. 1,483,798, February 12, 1924, to Green, Saunders, and British Dyes, cover the production of acetate silk azo dyes containing dialkyl-omega-sulfonic groups such as sodium ethylmethylaniline-omega-sulfonate, coupled with diazo compounds from *p*- and *m*-nitroaniline and dinitroaniline to obtain dyes giving red-orange, yellow, and bluish-red shades, respectively. These may also be used as acid dyes on animal fibers.

For example: 13.8 parts of *m*-nitroaniline are diazotized and the solution added to a cold concentrated aqueous solution of 23.7 parts of sodium ethylmethylaniline-omega-sulfonate. Sodium carbonate is added to faint alkalinity, when the dyestuff separates out. This dye readily hydrolyses in the dye bath and gives a golden yellow shade on acetate silk from either acid, neutral, or alkaline dye baths.

In British Patent No. 212,030, January 15, 1923, to Green, Saunders, and G. H. Frank, it is suggested to couple diazotized *p*-aminobenzeneazoanilinemethyl-omega-sulfonic acid, and other diaminoazomethyl-omega-sulfonic acids with *m*-phenylenediamine,

the former giving a red shade on acetate silk; or diazotized *p*-aminobenzeneazo-*B*-naphthylaminemethyl-omega-sulfonic acid with aminonaphtholdisulfonic acid (H-acid). Such dyes prepared from these or similar components, if without any sulfonic group attached to the benzene or naphthalene nucleus, may be used to dye acetate silk; while the similar dyes containing such sulfonic groups dye animal fibers. Many azo dyestuffs of the general formula $P.N:N.X.N:N.Y.NH.CH_2.SO_3H$ and $P.N:N.X.N:N.Y.N:N.Z.H.CH_2.SO_3H$, where P is a phenol, carboxyphenol, aminophenol, naphthol, aminonaphthol, dihydroxynaphthalene, or *m*-diamine, or a sulfonic acid thereof, may be prepared by diazotizing diaminoazomethyl-omega-sulfonic acids, and coupling the diazo compound so obtained with the above derivatives, the methyl-omega-sulfonate being unaffected.

For example: 37.8 parts of the sodium salt of the dyestuff obtained by combining *p*-nitrophenyldiazonium chloride with methyl-*B*-naphthylamine-omega-sulfonic acid and reducing with sodium sulfide, are diazotized in 2400 parts of water, and the product added to an alkaline solution of 42 parts of 81 per cent aminonaphthol and disulfonic acid H. After 12 hours stirring the solution is neutralized, heated to 45° C. (113° F.), and the dye salted out. This product dyes wool a blue shade from an acid bath.

According to British Patent No. 238,717, September 17, 1924, to W. H. Perkin, A. W. Fyfe, and the British Dyestuffs Corporation, the soluble *N*-methyl-omega-sulfonic acid of diaminochrysazin is prepared by treating the free base with formaldehyde bisulfite in the absence of a strong mineral acid. The dye may be crystallized or salted out and is washed and dried.

British Patent No. 252,922, July 8, 1925, to the British Dyestuffs Corporation, W. H. Perkin, A. W. Fyfe, and M. Mendoza, states that better yields of *N*-methyl-omega-sulfonic acid derivatives of 1, 4- and 1, 8-diaminoanthraquinone are obtained in the absence of strong mineral acids, by the process described for diaminochrysazin in British Patent No. 238,717, than by the process of British Patent No. 23,968 of 1899, although in the case of 1, 5-diaminoanthraquinone good results are only obtained in the presence of strong mineral acid. When the base is prepared in a

finely divided condition by solution in sulfuric acid and dilution with water, and then washed free of acid with water, very little more than the theoretical amount of formaldehyde-bisulfite is required. Thus, one gram molecule of 1, 4-diaminoanthraquinone is dissolved in 1600 grams of sulfuric acid and after 2 hours agitation at 100° C. is cooled and diluted with 20 liters of ice cold water. After decanting off the acid waste water and washing the precipitate on the filter, first with water and then with 2 per cent of soda to slight alkalinity, the paste is incorporated with a mixture of 2.5 molecules of 40 per cent sodium bisulfite and 2.5 molecules of 40 per cent formaldehyde. The mass is diluted with 500 cubic centimeters of water and stirred under a reflux for 8 hours at 100° C., when a liter of saturated salt solution is stirred in and the omega-sulfonate filtered off after cooling. In the case of the 1, 8-diaminoanthraquinone conversion is complete in about 12 hours.

United States Patent No. 1,609,702, December 7, 1926, to W. Duisberg, W. Hentrich, and L. Zeh, covers the use of amino-anthraquinone-*N*-methyl-omega-sulfonic acid compounds for dyeing acetate silk, ethylcellulose, and related compounds.

*References*

[1] A. G. Green and K. H. Saunders, *J. Soc. Dyers and Colourists 39,* 10-16 (1923), and *40,* 138-41 (1924).
[2] Bucherer and others, *Ber. 39,* 2796 and 2814.
[3] F. M. Rowe, *J. Soc. Dyers and Colourists 42,* 207-8 1926).
[4] British Dyestuffs Corporation, "Dyeing and Printing of Artificial Silks," (1926).

# CHAPTER XXI

## THE DISPERSOL TYPE OF DYES, OR DYEING BY COLLOIDAL SOLUBILIZATION OF THE DYESTUFF. THE S.R.A. DYES

THE dispersol type of dyestuffs or method of application, whichever we may care to call it, is the second entirely new group of dyestuffs to be developed especially for use upon acetate silk. Their announcement and appearance upon the market closely followed that of the Ionamines, the first products for this particular purpose. They are the result of considerable research and experience in England by the British Dyestuffs Corporation, the British Celanese Company, and others, in their search for dyestuffs adaptable to, or special methods of application particularly suited for, acetate silk. They are entirely the result of English research; and these two new products, the Ionamines and dispersol dyes, the latter group including the S.R.A., Celatene, Duranol, and Dispersol dyes, very clearly bring out the high type of research which appears to have become rather common in England since the war.

In the previous chapters the affinity of acetate silk for a large number of dyes, bases, etc., containing certain specific chemical groups or characteristics, has been repeatedly pointed out. Many, in fact, most of these compounds are not soluble in water, and the wide variety of methods which have been attempted in order to overcome this insolubility have been pointed out. The dispersol dyes are merely another attempt to overcome this insolubility of compounds having an affinity for acetate silk, but the *modus operandi* is entirely new, in that they are solubilized by physical methods and not by chemical methods, as in the usual procedure.

It is a heretofore unexpected fact, possibly not at all characteristic of dyeing acetate silk only, that certain compounds (dyestuffs) have a much greater affinity for acetate silk when in col-

loidal solution, possibly in even a rather coarse dispersion, than when they are in true solution. This is particularly the case where the compound is solubilized by means of chemical combination with some solubilizing reagent, such as the solubilization of certain bases by means of hydrochloric acid to form their hydrochlorides, or by sulfonation.

When the dyestuff is solubilized by the chemical method, as the sulfonate or hydrochloride, it is a case of the fiber's chemical and physical affinity for the basic portion of the dyestuff against that of the acid radicle and the water. Where the physical method of solubilization is used, such as in the dispersol process, there is no acid radicle affinity present in the dye bath, and the solubility of the dyestuff in water is usually so low that the compound is on the point of actual precipitation. As the attraction in this case is practicaly all one way, that is towards the fiber (acetate silk), it is not surprising that deeper shades are obtained than by the older chemical methods of solubilization, where at best, the dyestuff only comes to equilibrium between the aqueous-acid phase and the nonaqueous fiber phase.

Where the chemically solubilized dyestuff is highly hydrolyzed in the dye bath, as in the case of the Ionamines, we may expect the free basic portion of the hydrolyzed molecule to enter into either physical or, in this case, more probably chemical combination with the nonaqueous (fiber) phase, in which it appears to be more soluble than in water, and which is acidic in character, due to the acetate groups present. This in turn allows a further hydrolysis of the dyestuff, with a further absorption of free base, etc. Here there is probably an equilibrium reached between the aqueous-acid phase and nonaqueous-acid (fiber) phase, while with the physically solubilized dyestuff, there is more likely to be practically a complete exhaustion of the colloidal dyestuff up to the point of saturation of both the chemical and physical affinities of the fiber.

If we neutralize an aqueous base-hydrochloride solution with an alkali, such as sodium carbonate, the free base is precipitated as a colloidal or even coarser dispersion in the bath and this free

base is rapidly taken up by the acetate silk, as was mentioned in connection with the application of bases for the developed colors on acetate silk,[a] and we get much deeper shades than where we depend only upon the hydrolysis of the dyestuff (base-hydrochloride) to dye the fiber.

A particular case of this kind, in which the dispersion dyes acetate silk, while the solution does not, is shown by Spirit Red III (*o*-tolueneazo-*o*-tolueneazo-*B*-naphthol). When this dyestuff is dissolved in alcohol, the solution does not dye acetate silk, but upon pouring the alcoholic dyestuff solution into water, whereby the dyestuff is precipitated as a fine dispersion, it dyes acetate silk. For examples of the base-hydrochloride phenomenon, we have only to refer to the application of the bases to acetate silk for developed or azo colors. In the case of sulfonated dyes, the hydrolysis of the sulfonated color acid is probably so slight that the acetate silk is dyed very light shades in only a few cases.

Somewhat along the same line is the fact that acetate silk may be dyed a pure yellow shade by means of tartrazine from a bath containing (*a*) 0.75 per cent of sodium dioxytartrate dissolved with just sufficient hydrochloric acid, and (*b*) 1.3 per cent of phenylhydrazine dissolved in acetic acid. The two solutions (*a* and *b*) are mixed in the dye bath and the acetate silk immediately entered. It is turned for 10 minutes cold, the temperature gradually raised to 50° C. (122° F.), and the dyeing continued for 20 minutes. Any cotton present is not stained and the color on the acetate silk is fast to soaping at 40 to 50° C. (104 to 122° F.). By substituting *p*-nitrophenylhydrazine for the phenylhydrazine in *b*, an orange shade results. A terra-cotta color is obtained in a similar manner, in a single bath containing "nitrosamine" and 1, 2, 4-toluylenediamine in the presence of acetic acid.

In the same manner, many other comparatively insoluble coloring matters, such as Induline, Nigrosine, Rosaniline Base, Methyl Violet Base, as well as other compounds, not necessarily all bases, when in a more or less highly dispersed or colloidal condition, have a high affinity for acetate silk. The dispersol dyes offer a very easy and convenient method of obtaining these insoluble

[a] See Chapter XVI.

products in a dispersol or colloidal condition on a commercial scale, and undoubtedly many of the products previously mentioned as suitable dyestuffs, may be, or are, applied by this method.

In discussing the development of the S.R.A. dyes, Dr. Ellis,[1] who was a pioneer of this particular work, says that the experimental research upon the application of the various older and specially prepared dyestuffs to acetate silk developed a few rules very similar to those which led to the development of the Ionamines: (*a*) That the substantive affinity of a dyestuff for acetate silk is roughly proportional to the basicity of the dyestuff, and likewise approximately inversely proportional to its acidity or to its powers of salt formation with bases. This explains the comparatively high affinity of the basic dyes, many azo compounds, and the simple azo bases, as against the feeble or total lack of affinity by the acid and salt or cotton dyestuffs. Clavel[b] attempted to classify the various chemical groups usually found in dyestuffs in regard to their numerical preponderance over one another in dyeing acetate silk, however, among other things he failed to include in his generalizations the matter of the orientation of the groups in the dyestuff molecule, which is a very important factor.

(*b*) That the substantive affinity of a dyestuff for acetate silk is proportional to its molecular simplicity or inversely proportional to its molecular complexity or aggregation. Ellis states that whether chemical or physical solution theories be correct for the dyeing of acetate silk, this second generalization probably resolves itself into the question of simple "accessibility" of the dyestuff to the material of the filament, that is, the diffusion or non-diffusion through the semipermeable membrane of the filament surface. Apparently the size of the dyestuff molecule to some extent regulates the speed of diffusion of the dyestuff into the interior of the acetate silk.[c]

These rules, after much research and practical experience, led to the development of this new class of dyestuffs and method of dyeing acetate silk. It is a question just how many of the products used in this manner are really new compounds, but it is certain

[b] British Patent No. 182,830.
[c] See Chapter VIII.

that the method of application is new. In other words, it is possible that some or perhaps many of the dyes used are more or less well-known compounds, which are comparatively insoluble in water and other common solvents, but the physical method of solubilizing them for application to acetate silk is new. While the dispersol dyes were developed particularly for use on acetate silk, at least some of them are applicable to other fibers, as mentioned in some of the patents following. In fact many of these commercial products stain or dye wool and true silk more than may be desired where contrasting two color effects are wanted.

In developing the S.R.A. dyes, it was found that many comparatively water-insoluble commercial dyestuffs, bases, etc., as well as some new insoluble dyes were soluble in highly sulfonated castor oil or concentrated *S*ulfo*R*icinoleic *A*cid (from which the S.R.A. dyes receive their name), some of them apparently forming salts with the sulforicinoleic acid, which were soluble in excess of the solvent (acid), as in the case of S.R.A. Orange I. Most of them are also soluble in many other oleaginous compounds of salt-forming characteristics, such as the higher fatty acids and their salts, etc., as well as in many other organic compounds; and apparently in the case of the Duranols, Celatenes, and Direct Azonines, some such other solvent compound is used in place of the sulforicinoleic acid mentioned. Some of the recent patents along this line, as given in Chapter XXIII, may be of interest in this connection.

When once they are in solution, the solvent solution of the dyestuff may be placed directly in the dye bath without precipitating out the insoluble dyestuff. The dyestuff appears to remain in colloidal solution and the bath may be neutralized or even frequently made slightly alkaline to advantage. Under such conditions the dyestuffs pass through the ordinary dye-house cloth filter, or even through filter paper, and are readily taken up by the acetate silk.

In this manner it was found possible to dissolve and apply such insoluble products as the following to acetate silk: Nitrobenzeneazobenzeneazo-2-naphthol (Sudan III); Benzeneazodimethylaniline (Oil Yellow D); *m*-Nitrobenzeneazodiphenylamine; Nitrobenzeneazo-2-naphthol (Para-Red); 4-Nitro-2-methoxybenzene-1-azodiphenylamine; *p*-Acetamidobenzeneazo-1-naphthylamine; *p*-

Aminobenzeneazonaphthaleneazodimethylaniline; Aminoazonaphthalene; *p*-Aminobenzeneazophenylmethylpyrazolone; Dimethyl-*p*-aminophenyl-1, 4-naphthoquinonimine (Indophenol Blue); 1-Aminoanthraquinone (Yellow); 2-Aminoanthraquinone; 1-*p*-Tolylamino-4-hydroxyanthraquinone; Rosaniline base; Safrannine base; Methylene Blue base; *p*-nitroaniline; Benzidine; Dianisidine; Aminoazotoluene; and Di-*p*-methoxybenzoyldiaminoanthrarufin, as well as a host of other more or less similar products.

At the present time there is available a wide range of S.R.A., as well as other brands of dispersol dyes, which give direct shades on acetate silk ranging from lemon-yellow to dark blue or even black. There was also originally a group of products for diazotization and development on the fiber known as the Diazo Solamines.[2] These Solamines were later withdrawn and at present the only S.R.A. colors which it is usually necessary to diazotize and develop are S.R.A. Blacks III and IV. It is claimed that the dyeing of acetate silk by means of dispersol dyes is no more expensive and in some cases is cheaper, than the dyeing of cotton or the older rayons with colors of equal fastness.

In perfecting the series of dispersol dyes, the property of phototropism[d] again came into prominence, as in the development of the Ionamines, but the difficulty was again overcome satisfactorily. As before, the trouble was particularly prevalent on the greenish-yellows. While the exact constitution of the various S.R.A. dyes has not been divulged, probably at least one each of the S.R.A. and Celatene Yellows are nitroamino derivatives, and a review of the patent literature indicates that some of the others are simple azo and aminoazo compounds, possibly the yellows, oranges, and reds; while perhaps most of the violets and blues are of the anthraquinone series. Some of these are soluble in cold Turkey-red oil, etc., while others require heating. The S.R.A. dyes have been used in England since 1923.

The S.R.A. dyestuffs and their methods of application are controlled by the British Celanese Company and its branch, the American Cellulose and Chemical Company, and may only be used

[d] See Chapter VIII.

in conjunction with their product, Celanese. It is understood that they are now manufactured in America by the American Aniline Products Company. However, the Celatene and Duranol dyes[e] appear to give very similar results on Lustron, Rhodiaseta and Celanese. In fact it has been stated that nearly all substances capable of dyeing acetate silk may be applied to some extent by means of a dispersing agent. However, dyes having no direct affinity for this fiber, such as most direct and certain sulfonated acid dyes, cannot be applied by this method.

For certain purposes the use of a highly sulfonated castor oil in preparing the dispersol pastes is an advantage over the use of Turkey-red oil. When Turkey-red oil is used, only alkaline or neutral dye baths may be employed, but with the more highly sulfonated product, an acid bath may be employed and in dyeing acetate silk-wool unions in a combination dye bath this is certainly an advantage. Certain organic solvents, such as glycerol, epichlorohydrin, ethylene chlorohydrin, naphthalene-formaldehyde condensation products, etc., have been suggested as dispersing agents. Some of the solvents discussed under Solvent Dyeing in Chapter XVIII may also be applicable, as well as some of the new hydrogenated solvents, such as Tetraline, Hexalin, or Decalin. Some of these are now made in America by the Newport Chemical Works.

It is interesting to note that most dyes upon acetate silk conform more closely to simple rules governing the relationship of their chemical structure to their resistance to acids, alkalies, washing, and light, than is the case with any other fiber. Most of the dispersol dyes on the market have excellent fastness to the above as well as to soaping, ironing, volatility, perspiration, rubbing, phototropism, cross-dyeing of cotton or wool, domestic usage, weathering, etc. Table LI gives the colors obtained with the various S.R.A. dyes. It has been stated that all of the S.R.A. dyes are individual chemical compounds and that none of the following dyes are blends of two or more other dyes.

Table LII gives information regarding the fastness of the S.R.A. dyes on Celanese. The light fastness tests were made

[e] See Chapter No. XXII.

TABLE LI

COLOR OF THE S.R.A. DYES ON CELANESE

| | |
|---|---|
| S.R.A. Pure Yellow I | Lemon |
| S.R.A. Pure Yellow II | Greenish-Lemon |
| S.R.A. Golden Yellow VIII | Daffodil |
| S.R.A. Golden Yellow IX | Old Gold |
| *f*S.R.A. Fast Golden Yellow X | Golden Yellow |
| *f*S.R.A. Fast Golden Orange I | Marigold |
| *f*S.R.A. Fast Golden Orange III | Golden Orange |
| S.R.A. Orange I | Tangarine |
| S.R.A. Orange II | Brilliant Orange |
| S.R.A. Orange III | Brilliant Orange |
| S.R.A. Pink II | Pink |
| S.R.A. Red I | Scarlet Red |
| S.R.A. Red III | Crimson Red |
| S.R.A. Red V | Violet Red |
| *f*S.R.A. Fast Red VII | Red |
| *f*S.R.A. Fast Heliotrope I | Bright Heliotrope |
| *f*S.R.A. Fast Violet II | Brilliant Bluish-Violet |
| *f*S.R.A. Fast Blue III | Reddish-Blue |
| *f*S.R.A. Fast Blue IV | Pure Blue |
| S.R.A. Blue V | Deep Blue |
| S.R.A. Fast Black III (*B*-hydroxy-naphthoic acid) | Full Greenish-Black |
| S.R.A. Fast Black IV (*B*-hydroxy-naphthoic acid) | Full Bluish-Black |

In the above list the dyes marked *f* are particularly fast to light and compare in this respect with the vat dyes on cotton.

TABLE LII

FASTNESS PROPERTIES OF THE S.R.A. DYES ON CELANESE

| *Dye* | *Light* | *Soaping* | *Organic Acids* | *Alkalies* |
|---|---|---|---|---|
| S.R.A. Pure Yellow I | g. | g. | e. | e. |
| S.R.A. Pure Yellow II | g. | e. | e. | e. |
| S.R.A. Golden Yellow VIII | v.g. | v.g. | e. | e. |
| S.R.A. Golden Yellow IX | v.g. | v.g. | v.g. | e. |
| S.R.A. Golden Orange I | e. | v.g. | e. | f.g. |
| S.R.A. Orange I | v.g. | e. | e. | e. |
| S.R.A. Orange II | g. | v.g. | e. | e. |
| S.R.A. Pink II (recommended for underwear only) | f. | g. | g. | — |
| S.R.A. Red I | g. | e. | e. | e. |
| S.R.A. Red III | g. | e. | e. | e. |
| S.R.A. Red V | g. | e. | e. | e. |
| S.R.A. Heliotrope I | e. | v.g. | e. | e. |
| S.R.A. Violet II | v.g. | v.g. | e. | e. |
| S.R.A. Blue III | e. | v.g. | e. | e. |
| S.R.A. Blue IV | v.g. | v.g. | e. | e. |
| S.R.A. Blue V | g. | v.g. | e. | e. |
| S.R.A. Black IV (*B*-hydroxy-naphthoic acid) | e. | e. | e. | v.g. |

f = fair fastness; g = good; v.g. = very good; ex. = excellent.

against Indanthrene and Caledon vat dyes, and the washing tests against dyes such as the Chlorazol Fast, Diamine Fast, and Benzo Fast types. The fastness[7] to light of the S.R.A. dyes bearing the prefix "Fast" in Table LI is such that it is hardly necessary to use the method covered by British Patent No. 243,841[8] to increase their fastness to light.

The leading American authority on the S.R.A. dyes, Dort,[3] recommends the following combinations of S.R.A. dyes to obtain the various colors of best fastness to light:

*Violet*
S.R.A. Violet II
S.R.A. Heliotrope I
S.R.A. Blue IV

*Blue*
S.R.A. Blue III

*Green*
S.R.A. Golden Yellow VIII
S.R.A. Golden Yellow IX
S.R.A. Blue IV
S.R.A. Blue III

*Yellow*
S.R.A. Golden Yellow VIII

*Orange*
S.R.A. Golden Orange I

*Red*
S.R.A. Heliotrope I
S.R.A. Red III

*Grays, Browns and General Mode Shades*
S.R.A. Golden Yellow VIII
S.R.A. Heliotrope I
S.R.A. Blue III or
S.R.A. Golden Orange I
S.R.A. Red I
S.R.A. Blue III

*Navy*
S.R.A. Blue III
S.R.A. Golden Yellow IX
S.R.A. Red I

*Black*
S.R.A. Black IV developed with *B*-hydroxynaphthoic acid.

The best fastness to soaping is obtained with:

*Violet*
S.R.A. Violet II
S.R.A. Heliotrope I
S.R.A. Blue IV
S.R.A. Red V

*Blue*
S.R.A. Blue IV

*Green*
S.R.A. Pure Yellow II
S.R.A. Blue IV
S.R.A. Golden Yellow IX

*Yellow*
S.R.A. Pure Yellow II
S.R.A. Golden Yellow IX

*Orange*
S.R.A. Orange I
S.R.A. Golden Yellow IX

*Red*
S.R.A. Red I, III, or V
S.R.A. Heliotrope I

*Grays, Browns, and General Mode Shades*
S.R.A. Golden Yellow IX
S.R.A. Red I
S.R.A. Blue III or IV

*Navy*
S.R.A. Blue V
S.R.A. Red I or V
S.R.A. Golden Yellow IX

*Black*
S.R.A. Black IV developed with *B*-hydroxynaphthoic acid

[8]See Chapter XXII.

While S.R.A. Orange I has a very good fastness to light, when used in mixtures and exposed to very bright light, it is phototropic to some extent. It is therefore recommended only for pale mode shades. For full shades of brown, etc., it is best to use S.R.A. Orange II, Red I, or Heliotrope I. S.R.A. Heliotrope I in some cases has a slight fluorescent effect, which is not always desirable. Where only pale shades are required, S.R.A. Blues III and IV, Golden Orange I and Orange II, and Golden Yellows VIII or IX are widely used. Where medium shades are desired, the same blues, oranges and yellows are used. as well as S.R.A. Red I. For deep shades of navy blue and brown, S.R.A. Blue V, Golden Yellow VIII and IX, Orange II, and Reds I and V, are recommended. S.R.A. Orange III is extremely level dyeing and has good fastness to light and washing.

As a class most of the S.R.A. dyes show excellent fastness to washing and rubbing, while the fastness to acids, light and alkalies varies with the particular product used, as it does when this same compound is applied by any other method. With the exception of S.R.A. Blues I and II, these dyes withstand wool cross-dyeing very well and may be used in this manner.

At the present time the S.R.A. dyes are marketed only as pastes of the dyestuffs in the solubilizing medium, of a strength about equal to 10 per cent pastes of the usual dyestuffs for cotton. These pastes may be placed directly in the hot aqueous soapy or alkaline (ammoniacal) dye bath without any further treatment. They are applied by the usual direct dyeing methods, preferably in soapy dye baths, as an aid to penetration and leveling. Many of them may be applied cold without sacrificing fastness. They do not stain cotton or other artificial silks and may be mixed indiscriminately together, or may be applied in the same dye bath with suitable direct cotton dyes, despite the apparent chemical incompatability of the two groups. Sodium chloride or sulfate may be used in moderation to assist the cotton dye, but it does not benefit the dispersol dyes materially except for heavy shades, and it must not be present in sufficient quantity to cause salting out

of the soap, or to cause a precipitation of dye, which may become superficially fixed on the fiber and cause crocking.

*Method No. 74: The S.R.A. Dyes on Celanese.* The aqueous dye bath is usually prepared by adding about 0.5 to 1.5 grams of olive oil soap, or 1 or 2 cubic centimeters of Turkey-red oil or Celascour, per liter of dye bath, especially for pale shades and as an aid to penetration. In dissolving, or rather in diluting the dye pastes, it is best to add the fairly strong hot soap solution to the dye paste and then dilute this with hot water. Add this to the dye bath containing the balance of the soap. It is not necessary to heat the dye bath. Particular care must be used in dissolving S.R.A. Pure Yellow II, which is more difficult to bring into solution than the other members of the group.

The S.R.A. dyes are frequently applied by hand, using double sticks. They are also dyed on a suitable machine with porcelain rollers. Piece goods may be dyed in the jig. Bobbins, pins, cheeses, and beams are not usually attempted, as yet. For skein dyeing, a 25 to 1 dye bath is generally used, or for piece goods a 30 or 35 to 1 bath, but this may be varied according to the type of vat or machine. Copper dye vessels may be used. Materials of heavy or tight construction should be entered at a low temperature and worked for some time before heating the bath. It is also best to dye pale shades at a low temperature to insure evenness. The usual practice on the general run of goods is to dye for a half to one hour at 40 to 80° C. (104 to 176° F.) according to the particular dyes used, material being handled, and result desired. As a class the S.R.A. dyes feed onto Celanese most rapidly at about 76° C. (170° F.).

Most of the dye baths are clear, but a few are cloudy, even when heated. The most stable solutions appear to be those prepared cold and heated afterwards, instead of preparing the dye bath very hot. Some S.R.A. dye baths are so stable as to permit standing for several days without precipitation, but others will not. Most of these products dye level and are very fast.

Dort[4] recommends a dye bath containing approximately 1.5 grams of olive oil soap and 0.25 gram of soda ash, per liter, for

the application of the S.R.A. dyes. In no case should the amount of soda ash exceed 2 per cent, on the weight of the Celanese, in dye baths of the ordinary volume. The S.R.A. pastes should be dissolved in a boiling soap solution and filtered into the dye bath through cotton cloth. The addition of 4 to 8 cubic centimeters of Celascour, per liter of bath, aids in penetration and leveling. After applying the dispersol dyes, the goods should be rinsed with water at 45° C. (113° F.), followed with cold water and then soaped. It is quite common to find some difference in the shade of a dyed fabric before and after dyeing, but on Celanese this difference in shade appears to be greater than on most other materials.

As the S.R.A. dyes are applied in a soapy dye bath, soft water is absolutely essential for their successful application. Colloidal solutions are inclined to be affected to a considerable extent by what we are sometimes inclined to consider minor factors, and for this reason it is always best to avoid undue complications and the entry of any unusual factors into the application of dyes by the colloidal solubilization or dispersol method. In many instances emulsions are affected by electrolytes, temperatures, etc., in such a way as to considerably influence the size of the colloidal aggregate. Such factors may have a considerable bearing upon the shade obtained by a given formula.

Greenhalgh[5] states that hard water may also have such a deleterious effect upon dispersol dyes containing anthraquinone or its substituted homologues as to render them valueless from a tinctorial standpoint. He points out that in many cases it is not at all satisfactory to attempt to soften the water in the dye bath itself.

*Method No. 75: Topping the S.R.A. Dyes with Basic Dyes.* The dispersol dyes may be topped with basic dyes in the same manner as the substantive dyes are topped on cotton. Another method of topping, which is particularly adapted for use in connection with the dispersol dyes, is to dissolve the free color base of the common basic dyes, such as Rosaniline Base, Methyl Violet Base, Saffranine Base, Quinoline Yellow, Indophenol, etc., in 10

times its weight of Turkey-red oil. This solution is diluted with boiling 5 per cent soap solution, the whole boiled again, and may then be added to the dispersol dye bath and applied concurrently with the principal dispersol dyestuff. This of course avoids a separate topping operation and probably gives much better results.

### *The S.R.A. Blacks*

The S.R.A. Blacks are the only members of this group which require diazotization and development on the fiber. S.R.A. Black III gives a greenish-black when diazotized and developed with *B*-hydroxynaphthoic acid. Black IV is a newer dye, is extremely fast and gives a full bluish-black with *B*-hydroxynaphthoic acid. Since it also gives a good black with *m*-toluylenediamine, it is very suitable for use in dyeing acetate silk-cotton hosiery. It may be dyed in the same dye bath with a diazotizable cotton black to give a solid black shade upon development.

S.R.A. Black IV is not recommended for use as a direct dye, but gives a variety of colors with different developers, as shown in Table LIII. The light fastness of these developed colors vary somewhat, so that they should be tested before use. In developing the S.R.A. Blacks on Celanese, it is recommended to diazotize and develop the base by the usual method for other fibers and colors, except that the developing bath should be hot, and when *B*-hydroxynaphthoic acid is used as the developer, the developing bath should be distinctly acid to litmus. The addition of glue to the bath, while not essential, is usually advantageous. Method 76 covers the process.

TABLE LIII.

Colors Obtained by Developing S.R.A. Black IV.

| *Developer* | *Color* |
|---|---|
| Direct (not developed) | Orange Brown |
| *m*-Phenylenediamine | Brownish-Black |
| Dimethylaniline | Deep Purplish-Maroon |
| Resorcinol | Maroon |
| Naphthol AS | Reddish-Blue |
| *B*-Naphthol | Deep Purple |
| *B*-Hydroxynaphthoic Acid | Bluish-Black |
| *m*-Toluylenediamine | Black |
| S.R.A. Black Developer HY Special | Black |

*Method No. 76: S.R.A. Black IV on Celanese.* Dye at 80° C. (176° F.) in a 30 to 1 bath containing 15 or 20 per cent of S.R.A. Black IV and 1 gram per liter of olive oil soap for an hour and a half. The direct color will be a brownish orange. Rinse well and diazotize for a half hour in a 15 to 1 dye bath containing 5 per cent of sodium nitrite and 16 per cent of 28° Tw. (1.14 sp. gr.) hydrochloric acid. Rinse again and immediately enter into a 30 to 1 developing bath at 35° C. (95° F.) containing 2.5 per cent of *B*-hydroxynaphthoic acid, 0.6 per cent of caustic soda, 3 per cent of glue, and 3 per cent of 100 per cent acetic acid. During a half hour raise the temperature of the developing bath to 60° C. (140° F.) and continue the development for about a half to three-quarters of an hour at this temperature. Finish by a light soaping. Where a greener tone of black is desired, it may be shaded with S.R.A. Golden Orange I. A jet black may be obtained with 16 per cent of S.R.A. Black IV and 4 per cent of Orange I, developed as above. Care must be taken to insure complete development of the dye or the black color will redden on washing. In applying black to Celanese, it is important to develop immediately after the diazotization, in not too dilute a bath. The addition of the acetic acid is an important point which must not be neglected.

## *Compound Shades*

The dyeing of compound shades on any fiber is usually much more of a problem than the application of simple shades. As in the dyeing of compound shades on any other fiber, a complete knowledge of the characteristics and peculiarities of each individual component dyestuff is a prime requisite for success. Greenhalgh[6] points out that this difficulty is particularly prevalent in the application of greens, fawns, and mole shades, with dispersol dyes, and says that unless very close temperature control is used in the dye bath, it is impossible to match shades exactly. As an instance of this he mentions the production of a Jade Green shade on Celanese with S.R.A. Blue IV and Golden Yellow VIII. "At certain stages in the dyeing operation of this shade, the result has a tendency to exhibit a yellowish cast, particularly if the dyeing is

done at a temperature below that of 65° C. (149° F.), but on raising the temperature to a higher degree this yellowness disappears, giving fuller tones of blue. If at this juncture an addition of Yellow be made to the dye bath, the bluenss is not diminished but on the other hand seems to be accentuated, whereas if the temperature be lowered the preponderance of yellow is again manifested."

In applying the dispersol dyes to acetate silk, which in many ways acts just like a simple solution of the dyestuff in the fiber, each dyestuff apparently has a definite temperature at which it exhibits a maximum reactivity for, or solubility in, the fiber. In a mixture with other dyes of the same class, this may not at all coincide with the maximum reactivity temperature of the other components of the mixture. Undoubtedly these same factors hold good in the application of the developing or azo color bases to acetate silk from neutralized solutions of their hydrochlorides, etc.

The following formulas for various compound shades with the S.R.A. dyes will give an excellent idea of what is being recommended for and used on Celanese:

*Green*

A-1:
6.0% S.R.A. Blue IV paste and
10.0% S.R.A. Golden Yellow VIII paste.

A-2: Apple Green
0.95% S.R.A. Pure Yellow II paste and
0.12% S.R.A. Blue IV paste.
Enter cold and raise to 75° C. (167° F.) in an hour.

A-3: Bright Green
16.0% S.R.A. Golden Yellow VIII paste and
7.0% S.R.A. Blue IV paste.

A-4: Almond Green
0.6% S.R.A. Blue III paste and
2.5% S.R.A. Golden Yellow IX paste.

A-5: Dull Green
3.0% S.R.A. Blue II paste and
8.0% S.R.A. Pure Yellow I paste.
Enter cold and dye at 70 or 75° C. (158 or 167° F.) for an hour.

A-6: Pale Greenish Gold
4.0% S.R.A. Golden Orange I paste and
0.8% S.R.A. Blue III paste.
This may be shaded with S.R.A. Blue III and Orange I, if desired.

*Putty*

A-7:
3.0% S.R.A. Blue II paste,
0.2% S.R.A. Orange I paste, and
1.5% S.R.A. Golden Orange VIII paste.
Enter cold and dye at 75° C. (167° F.) for an hour.

A-8:
0.4 % S.R.A. Blue III paste,
0.5 % S.R.A. Golden Yellow IX paste, and
0.06% S.R.A. Heliotrope I paste.

A-9: Light Tangarine
3.5% S.R.A. Golden Orange IX paste and
2.75 S.R.A. Red I paste.
Enter cold and raise to 80° C. (176° F.) in three-quarters of an hour and dye at this temperature for three-quarters of an hour.

A-10: Tangarine
4.0% S.R.A. Orange I paste and
0.7% S.R.A. Red I paste.
Enter cold and dye at 60° C. (140° F.) for an hour.

A-11: Puce
10.0% S.R.A. Red V paste and
1.5% S.R.A. Orange I paste.

A-12: Pale Reddish Gold
1.0% S.R.A. Golden Yellow IX paste and
0.2% S.R.A. Heliotrope I paste.
Enter cold and raise to 70° C. (158° F.) for an hour or an hour and a half.

A-13: London Lavender
0.6 % S.R.A. Heliotrope I paste and
0.06% S.R.A. Blue III paste.

*Reds*

A-14: P.O. Red
4.0% S.R.A. Orange I paste and
2.0% S.R.A. Red I paste, with
1.1% Rosaniline Base NSF 100% (See Method No. 75).
Enter cold and raise to 75° C. (167° F.) in 2 hours.

A-15: Brick
0.25% S.R.A. Orange I paste and
0.25% S.R.A. Red I paste.

A-16: Light Strawberry
1.5% S.R.A. Red V paste and
0.2% S.R.A. Orange I paste.

A-17: Deep Crimson
1.2% S.R.A. Red V paste and
6.0% S.R.A. Red III paste.

A-18: Reddish-Violet
5.0% S.R.A. Violet II paste and
5.0% S.R.A. Heliotrope I paste.
Enter cold and raise to 75° C. (167° F.) in an hour and a half.

A-19: Violet
8.0% S.R.A. Blue I paste and
8.0% S.R.A. Red V paste.
Enter cold and dye at 75° C. (167° F.) for an hour and a half.

*Fawn*

A-20:
1.3% S.R.A. Blue III paste,
0.5% S.R.A. Golden Orange VIII paste, and
0.6% S.R.A. Golden Orange I paste.
Enter cold and raise to 70° C. (158° F.) in an hour and a half.

A-21:
0.4 % S.R.A. Blue III paste,
0.65% S.R.A. Golden Yellow IX paste, and
0.04% S.R.A. Red I paste.
Enter cold and raise to 75° C. (167° F.) in an hour and a half.

*Brown*

A-22:
8.0% S.R.A. Blue III paste,
8.0% S.R.A. Orange I paste, and
2.0% S.R.A. Golden Yellow VIII paste.
Enter cold and dye at 80° C. (176° F.) for an hour and three-quarters.

A-23:
3.0% S.R.A. Red I paste,
10.0% S.R.A. Blue I paste, and
20.0% S.R.A. Golden Orange VIII paste.
Enter cold and dye at 80° C. (176° F.) for an hour and three-quarters.

A-24: Leaf Brown
1.5 % S.R.A. Golden Orange I paste,
0.3 % S.R.A. Blue III paste, and
0.25% S.R.A. Red I paste.
Dye at 80° C. (176° F.) for an hour.

A-25: Dark Beaver
1.4% S.R.A. Blue III paste,
4.6% S.R.A. Golden Yellow VIII paste, and
0.3% S.R.A. Red I paste.
Enter cold and raise to 80° C. (176° F.) in three-quarters of an hour and dye at this temperature for three-quarters of an hour.

A-26: Golden Brown
12.0% S.R.A. Golden Orange I paste and
2.0% S.R.A. Blue III paste.

A-27: Golden Brown
7.0% S.R.A. Orange II paste,
2.5% S.R.A. Golden Yellow VIII paste, and
2.0% S.R.A. Blue III paste.
Enter cold and dye at 75° C. (167° F.) for an hour and a half.

A-28: Reseda
3.8% S.R.A. Golden Yellow IX paste,
1.0% S.R.A. Golden Orange I paste, and
2.5% S.R.A. Blue IV paste.
Enter cold and raise to 80° C. (176° F.) in an hour and a half.

A-29: Nigger
4.0% S.R.A. Golden Yellow VIII paste,
6.0% S.R.A. Orange II or Red I paste, and
12.0% S.R.A. Blue III paste.
Enter cold and raise to 80° C. (176° F.) in 2 hours.

A-30: Cordovan
0.9% S.R.A. Red I paste,
0.6% S.R.A. Golden Yellow IX paste, and
0.9% S.R.A. Blue III paste.

A-31: Bronze
3.0% S.R.A. Golden Yellow III paste,
0.5% S.R.A. Red I paste, and
2.5% S.R.A. Blue III paste.

A-32: Flame
0.5% S.R.A. Golden Yellow VIII paste, and
2.0% S.R.A. Orange I paste.

A-33: Whirlpool
16.5% S.R.A. Blue IV paste and
3.2% S.R.A. Pure Yellow II paste.
Enter cold and raise to 75° C. (167° F.) in 2 hours.

A-34: Navy Blue
25. % S.R.A. Blue III paste,
4 % S.R.A. Golden Yellow IX paste, and
4 % S.R.A. Orange II paste.
Enter cold, raise to 80° C. (176° F.) in an hour and dye at this temperature for an hour.

A-35: Pongee
0.1 % S.R.A. Orange I paste,
0.24 % S.R.A. Golden Yellow IX paste, and
0.244% S.R.A. Blue III paste.

*Grays*

A-36:
2.0 % S.R.A. Blue III paste,
0.3 % S.R.A. Golden Orange paste, and
0.15% S.R.A. Orange I paste.
Enter cold and dye at 75° C. (167° F.) for an hour.

A-37:
0.75% S.R.A. Pure Yellow I paste,
3.5 % S.R.A. Blue I paste, and
0.75% S.R.A. Orange I paste.
Enter cold and dye at 60° C. (140° F.) for an hour.

A-38:
1.15% S.R.A. Blue III paste,
0.21% S.R.A. Orange I paste, and
0.22% S.R.A. Golden Yellow VIII paste.
Dye at 80° C. (176° F.) for an hour.

A-39: Medium Gray
1.0 % S.R.A. Blue III paste,
0.25% S.R.A. Golden Yellow IX paste, and
0.08% S.R.A. Orange I paste.
Enter cold and raise to 80° C. (176° F.) in three-quarters of an hour, and dye for three-quarters of an hour.

A-40: Light Gray
0.036% S.R.A. Golden Yellow IX paste,
0.016% S.R.A. Blue IV paste, and
0.018% S.R.A. Heliotrope I paste.

A-41: Dark Gray
0.17% S.R.A. Golden Yellow IX paste,
0.08% S.R.A. Blue IV paste, and
0.1 % S.R.A. Heliotrope I paste.

Prepare the dye bath with 1 gram of olive oil soap and 0.25 gram of sodium carbonate per liter. Dye at 80° C. (176° F.) for three-quarters of an hour. After dyeing, soap for a half-hour in a bath containing 2 grams of soap and 2 cubic centimeters of ammonia per liter at 60° C. (140° F.).

A-42: Champagne
2.0 % S.R.A. Golden Yellow IX paste and
0.015% S.R.A. Blue III paste.

A-43: Mauve
0.7% S.R.A. Heliotrope I paste and
0.7% S.R.A. Violet I paste.

A-44: Nude
0.075% S.R.A. Golden Yellow IX paste and
0.005% S.R.A. Red I paste.

A-45: Sunburn
0.1 % S.R.A. Blue III paste,
0.02% S.R.A. Red I paste, and
0.08% S.R.A. Golden Yellow IX paste.

A-46: Silver
0.3 % S.R.A. Blue III paste,
0.08% S.R.A. Golden Yellow VIII paste, and
0.03% S.R.A. Heliotrope I paste.

*References*

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[2] C. E. Mullin, *American Dyestuff Reporter 14,* 554 (1925).
[3] R. G. Dort, *Chemicals 24,* No. 19, 19-22 (1925).
[4] R. G. Dort, *American Dyestuff Reporter 15,* 260 (1926).
[5] E. Greenhalgh, *Dyer & Calico Printer 55,* 106 (1926).
[6] E. Greenhalgh, *Dyer & Calico Printer 55,* 107 (1926).
[7] G. H. Ellis, *J. Soc. Dyers and Colourists 42,* 184-6 (1926).

# CHAPTER XXII

## THE CELATENE, DURANOL, DISPERSOL, DIRECT AZONINE, CIBACETE, CELANTHRENE, CELLACETE, AND OTHER DYES FOR ACETATE SILK

*Their Properties and Application. Increasing the Light Fastness of Colors on Acetate Silk.*

From the foregoing it may be assumed that the S.R.A. dyes are the only members of the dispersol group. However, this is not the case as we have several other very important brands of dyestuffs coming under this classification. While it is true that the S.R.A. dyes were the first products belonging to this class to be offered commercially, the Duranol dyes of the British Dyestuffs Corporation and the Celatene dyes of Scottish Dyes, Ltd., are very important members of this group.

Both the Celatene and Duranol dyes are prepared dispersions of comparatively water-insoluble compounds in the form of pastes, which resemble the S.R.A. dyes to some extent. No doubt some of the Duranol and Celatene dyes are very similar products to certain S.R.A. dyes. It has been stated that some members of all three brands (S.R.A., Duranol and Celatene) are azo compounds, while others are anthraquinone derivatives. Casten[1] states that the Duranol dyes are derivatives of chloro- or bromoanthraquinone condensed with anthranilic acid. From the literature and patents on the subject, as well as the properties of the products themselves, the Celatene dyes also appear to consist largely of anthraquinone compounds.

Another point of wide difference between the S.R.A. dyes on the one hand and the Celatene and Duranol dyes on the other, is in the composition of the dispersing or solubilizing medium. We have seen how sulforicinoleic acid and soap are used in solubilizing the S.R.A. dyes, but in the preparation of the Duranol and Celatene pastes, some nonsoapy medium is used. In some dyeing processes, as for instance where true silk or wool are present, this

nonsoapy dispersing medium may offer some advantages in that the Celatene and Duranol dyes may be applied from dye baths without the addition of any other chemicals, *i.e.*, alkalies or soap, and yet the shade is not affected by the presence of either alkalies, soap, salt, Turkey-red oil, or the other usual assistants used in the dye bath. These nonsoapy dispersions have an excellent stability in the dye bath and show no tendency to precipitate.

### *The Duranol Dyes*

The Duranol dyes are the products of the British Dyestuffs Corporation and are marketed in America by the Dyestuffs Corporation of America, of Boston. At the present time they offer Duranol Orange G, Duranol Red G, Duranol Red 2B, Duranol Blue G, Duranol Violet 2R, and a Duranol Black. These are sold as 10 per cent pastes which only require dilution with water to the desired strength for application. They may also be printed on acetate silk, as discussed under printing in Chapter XXIV. Neither the Duranol or Dispersol dyes have any affinity for cotton but they all stain wool and true silk. The Duranol dyes are applied to acetate silk by Method No. 77. They have excellent fastness to washing, alkalies, acids, perspiration, rubbing, and particularly to light; good fastness to cross-dyeing and the usual fulling.

*Method No. 77: The Duranols on Acetate Silk.* The dye bath is prepared by diluting the Duranol paste with warm water. The acetate silk is entered cold and the temperature slowly raised to 75 or 80° C. (167 or 176° F.) for a half to one hour. The different members of the group may be mixed together in the dye bath. They level well and may be used in the same dye bath with most direct and acid dyes, in the presence of either acids, alkalies, salt, soap, or Turkey-red oil. While the latter two aid in leveling and penetrating, they also retard the exhaustion and for this reason should not be present to the extent of more than two or three parts, per part of dyestuff. Duranol Blue G does not exhaust as completely as the other Duranol dyes and therefore for full shades may require a somewhat longer time at the maximum temperature.[3]

### *Dispersol Yellow 3G Paste*

The British Dyestuffs Corporation also offer another member of the dispersol class of dyestuffs for acetate silk, Dispersol Yellow 3G Paste. This gives a brilliant greenish-yellow shade which is not phototropic, when applied by Method No. 77, as for the Duranols. Its fastness properties in general are similar to those of the Duranols, except to light, in which case it is not equal to the members of the other group.

### *The Celatene Dyes*

The Celatene dyes of that very progressive company, Scottish Dyes, are one of the most successful brands of dispersol dyes on the market. As previously mentioned, they are largely anthraquinone derivatives dispersed by means of a nonsoapy medium. In the discussion on the theory of acetate silk dyeing, the high affinity of many anthraquinone compounds for acetate silk was mentioned, and this may account to some extent for the fastness properties of the Celatene dyes on acetate silk. Probably the patents, which are reviewed in Chapter XXIII, give more real information regarding their constitution than any other source.

At the present time, the following colors are available: Celatene Yellow, Celatene Fast Light Yellow, Celatene Orange, Celatene Gold Orange, Celatene Fast Light Brown, Celatene Brilliant Red, Celatene Red B, Celatene Scarlet, Celatene Red Violet, Celatene Brilliant Violet B and 2B, Celatene Blue, Celatene Brilliant Blue and Celatene Black. These give clear, brilliant shades of excellent fastness to light.

The Celatenes will dye acetate silk under almost any condition which does not destroy the fiber. For instance they may be applied either in a neutral, acid, or alkaline (soda ash) bath, with or without Glauber's salt, in long or short baths, at from room temperature up to 75 or 80° C. (167 to 176° F.), with good results, only the exhaustion varying somewhat under the different conditions, as would be expected. For certain purposes, such as dyeing knit goods, a short bath in a jig is used, but for yarns, longer baths are generally used. Method No. 78 gives a general

idea of the process as recommended by the manufacturers. It is interesting to note that these products are also applicable to many fibers other than acetate silk.

*Method No. 78: The Celatene Dyes on Acetate Silk.* The necessary quantity of dyestuff paste is added directly to the bath without any other addition and the bath warmed to about 40 to 60° C. (104 to 140° F.). While the bath may not be clear at the start, this does not in any way interfere with the results. The well wet-out material should be entered into this warm 20 or 40 to 1 dye bath, according to the type of dyeing apparatus used, the shorter baths giving much better exhaustion. During about a half-hour the temperature is raised to from 70 to 85° C. (158 to 185° F.) while working the goods, until the desired shade is obtained. The exhaustion is usually fairly complete in a half to three-quarters of an hour. Where very dark shades are desired, it is best to use a standing bath and dye to shade, refreshing the bath with about five-eighths of the starting weight of dyestuff. The dyed material should be rinsed well and dried; or better yet, soaped at 60° C. (140° F.) in a 1 per cent soap bath, to render the shade slightly brighter and faster to rubbing, before drying. While these dyes have excellent leveling properties, in case of difficulty the temperature of the dye bath may be lowered, for instance to 30° C. (87° F.) and a longer time given. It has been stated[4] that acetic acid will aid the exhaustion of certain of these dyes, while in others the exhaustion is retarded. A soluble oil, in the absence of acetic acid, usually brightens the shade of the dyed fiber but the remaining oil is usually difficult to remove from the material, and any oil not removed may give the fiber a rather cold feel.

The application of these dyes depends upon their slight solubility in water, together with their great affinity for acetate silk. The small amount of dyestuff in solution when the goods enter the dye bath is quickly absorbed by the acetate silk, thus allowing more of the suspended dye to dissolve and be absorbed in its turn, until almost complete exhaustion of the dye bath takes place. Two per cent of Celatene Red Violet will give a medium shade but as much as 20 or even 30 per cent (black) of some of these dyes are required for heavy shades. Table LIV gives some information on

the fastness of a few of the Celatene dyes. It is interesting to note that Celatene Fast Light Yellow is faster to light on acetate silk than any of the vat yellows on cotton.

These fastness tests were conducted as follows: *Bleaching:* The dyed yarn was bleached for an hour in a fresh 2°Tw. bleach bath. *Hot pressing:* Dyed yarn sample was pressed between 2 pieces of mercerized cloth with a hot iron. The *perspiration* test was the same as for vat colors on cotton, using both acid and alkaline perspiration. *Rubbing* tests were made both wet and dry. *Cross-dyeing:* *(a)* Effect of alkaline hydrosulfite. *(b)* Effect of 20 per cent sodium sulfate and 2 per cent sulfuric acid at 75° C. (167° F.) for an hour. (*c*) Effect of 1 per cent bichromate at 75° C. for an hour. *Washing* test. (*a*) One per cent soap at 60° C. (146° F.), in 3 periods of 2 hours each, or a total of 6 hours. (*b*) One per cent soap at 80° C. (176° F.) in 3 periods of 2 hours each, or a total of 6 hours. The *light* test was to sunlight, under glass. The *leveling* test was made by entering a plaited hank of acetate silk into the dye bath at 75° C. (167° F.) and allowing it to remain untouched for an hour.

TABLE LIV

FASTNESS OF CELATENE COLORS ON ACETATE SILK

| *Tests* | *Light* | *Washing Tests* Loss in depth | Bleeding on viscose and cotton | Bleeding on wool and silk | Bleeding on Celanese | *Bleaching* | *Street Mud* |
|---|---|---|---|---|---|---|---|
| Cel. Yellow | m/p. | g. | ex. | ex. | g. | ex. | ex. |
| " Red B. | v.g. | m. | v.g. | v.g. | m. | ex. | ex |
| " Bril. Violet B. | ex. | v.g. | v.g. | v.g. | g. | ex. | ex |
| " Red Violet | ex. | g. | v.g. | v.g. | m. | ex. | ex. |
| " Bril. Violet 2R | ex. | v.g. | ex. | v.g. | v.g. | v.g. | ex. |
| " Orange | v.g./g. | g. | ex. | g. | m. | ex. | ex. |
| " Blue | g/m. | v.g. | v.g. | v.g. | ex. | g. | v.g. |
| " Fast Light Yellow | ex. | | | | | | |
| " Fast Light Brown | ex. | | | | | | |

| *Tests* | *Milling* Loss in depth | Bleeding | *Cross-Dyeing* Alkaline Hyrods | Glaubers Acid | Chrome and Acid | *Rubbing* Wet | Dry | *Perspiration* Alkaline | Acid |
|---|---|---|---|---|---|---|---|---|---|
| Cel. Yellow | v.g. | ex. | p | ex. | v.g. | v.g. | ex. | ex. | ex. |
| " Red B. | v.g. | g. | p. | g. | ex. | ex./v.g. | ex./v.g. | v.g. | v.g. |
| " Bril. Violet B. | ex. | v.g. | p. | v.g. | v.g. | ex. | ex. | v.g. | v.g. |
| " Red Violet | ex. | ex. | p. | v.g. | v.g. | ex. | ex. | v.g. | v.g. |
| " Bril. Violet 2R | g. | ex. | p. | v.g. | p. | ex. | ex. | ex. | ex. |
| " Orange | v.g. | g. | p. | v.g. | v.g. | ex./v.g. | v.g. | ex. | ex. |
| " Blue | ex. | v.g. | g. | ex. | ex. | v.g. | v.g. | ex. | g. |

p. = poor fastness; m. = medium; g. = good; v.g. = very good; ex. = excellent.

| Tests | *Hot Pressing* Change in shade | *Hot Pressing* Staining | *Acid Spotting* $H_2SO_4$ | *Acid Spotting* Acetic | *Leveling* |
|---|---|---|---|---|---|
| Cel. Yellow | ex. | ex. | ex. | ex. | ex. |
| " Red B. | ex. | v.g. | ex. | ex. | ex. |
| " Bril. Violet B. | ex. | g. | ex. | ex. | v g. |
| " Red Violet | ex. | g. | ex. | ex. | ex. |
| " Bril. Violet 2 R. | ex. | g. | ex. | ex. | v.g. |
| " Orange | ex. | v.g. | ex. | ex. | ex. |
| " Blue | ex. | ex./v.g. | ex. | ex. | ex. |

Celatene Fast Light Yellow, Cel. Fast Light Brown, and Cel. Orange redden on soaping, but this is removed by a weak sour.

Celatene Red Violet is the fastest member of the series to light and after 6 months' exposure of light shades, only a slight fading was noticed, while darker shades required twice this period of exposure. This is equal to that of the best vat dyes on cotton. Celatene Fast Light Yellow and Fast Light Brown approach this fastness, and even tints of the Yellow are unchanged after 6 months' exposure. Heavier shades are reddened by 10 months' exposure. Under the same exposure the brown shows only a slight fading, which is equal to any of the fast vat colors of similar shade. The light fastness of Celatene Brilliant Violet 2R is similar to that of Caledon Brilliant Purple RR (Indanthrene Brilliant Violet RR or Ponsol Violet RR) on cotton. The shade fades slightly and is redder. From this we might assume that the composition of the Celatene Brilliant Violet 2R is similar to that of the Caledon dye, which is dichloroisodibenzanthrone.

Celatene Brilliant Violet B withstands about 6 months' exposure, when it becomes redder. This compares favorably with Caledon, Algol or Indanthrene Brilliant Violet R (4, 8-dianisoyl-diamino-1, 5-dihydroxyanthraquinone) on cotton. Celatene Orange is browner after 2 months' exposure but then remains almost unchanged. Medium shades of Celatene Red B and Blue are not faded by several months' exposure. Celatene Yellow and Black are the poorest of the products, as regards light fastness, as both are distinctly browner after a month's exposure. Light shades of these colors have an excellent fastness to washing, but deeper shades are not as good. All are fast to chlorine except Celatene Blue, but this shade is restored by treatment with a dilute solution of hydrosulfite.

*The Azonine Direct Dyes and Azonine SF*

Another brand of dispersol dyes are the Direct Azonines of the Cassella Company. This is the second group of Azonine dyes to be considered as we also had a group under this brand in the developed colors. The Direct Azonines are entirely different from those previously discussed and are suitably prepared dispersions of insoluble dyestuffs which have an affinity for acetate silk. In applying these dyes the acetate silk should be scoured as in Method No. 5 and is then ready to enter the dye bath, prepared as in Method No. 79. While Azonine SF is diazotized and developed on the fiber, it is applied by the dispersol method. Also see the application of Azonine bases for development by means of a tetralin-soap bath, as in Method No. 65 under the Developed Colors, Chapter XVII.

*Method No. 79: The Direct Azonines on Acetate Silk.* Azonine Direct Yellow 2R paste, Azonine Direct Red G paste, Azonine Direct Violet R paste and Azonine Direct Blue B paste, are dissolved with the addition of approximately the same weight of soap as of dye in boiling very soft water. This concentrated solution is strained into the dye bath, previously heated to 60 or 70° C. (140 or 160° F.). For light shades it is advantageous to add sufficient soap to the bath to bring the total soap content up to 6 to 8 ounces per 10 gallons of dye bath. In case hard water is used, it is best to replace the soap with monopol soap or a similar product which is not precipitated in hard water. The dyes level well and the wet out acetate silk is usually entered into the dye bath at about 60 to 70° C. (140 to 160° F.) and dyed at this temperature for 30 or 40 minutes, without any further addition, and then rinsed well.

*Method No. 80: Azonine SF on Acetate Silk.* Azonine SF is dissolved in boiling water containing twice the weight of soap as of dye to be dissolved. This solution is strained into the dye bath previously heated to 60 to 70° C. (140 to 160° F.). The scoured acetate silk is entered at this temperature, worked for about 45 minutes, and rinsed.

*Method No. 80-A: Diazotizing SF on Acetate Silk.* Diazotize for 15 or 20 minutes in a cold bath containing 2.5 ounces of

sodium nitrite and 8 ounces of 34° Tw. hydrochloric acid, per 10 gallons of liquor. Rinse well and develop immediately.

*Method No. 80-B: Developing Azonine SF on Acetate Silk.* The developing bath is prepared by first dissolving a pound of Developer ON in 2 to 3 gallons of water containing 2 pounds of sodium acetate. This concentrated solution is added to the developing bath in such proportions that when ready for use it will contain about 2.5 ounces of Developer ON per 10 gallons of bath. In other words, 1 pound of Developer ON and 2 pounds of sodium acetate will make up a developing bath of 64 gallons. The wet, rinsed, diazotized acetate silk is immediately entered into this bath at 45 to 50° C. (113 to 122° F.) worked for 20 or 30 minutes and then rinsed well.

TABLE LV
THE DIRECT AZONINES ON ACETATE SILK

| *Color* | *Dyes* |
|---|---|
| Greenish-Yellow | 0.75% Azonine Direct Yellow 2R paste and<br>0.14% Azonine Direct Blue B paste. |
| Medium Bluish-Gray | 0.7% Azonine Direct Yellow 2R paste,<br>1.6% Azonine Direct Blue B paste, and<br>0.2% Azonine Direct Red G paste. |
| Medium Reddish-Tan | 0.14% Azonine Direct Yellow 2R paste,<br>0.7% Azonine Direct Blue B paste, and<br>0.4% Azonine Direct Red G paste. |
| Light Tan | 0.38% Azonine Direct Yellow 2R paste,<br>0.15% Azonine Direct Blue B paste, and<br>0.3% Azonine Direct Red G paste. |
| Medium Brownish-Tan | 4.0% Azonine Direct Yellow 2R paste,<br>2.2% Azonine Direct Blue B paste, and<br>0.7% Azonine Direct Red G paste. |
| Dark Chestnut Brown | 3.3% Azonine Direct Yellow 2R paste,<br>3.3% Azonine Direct Blue B paste, and<br>1.7% Azonine Direct Red G paste. |
| Medium Green | 3.3% Azonine Direct Yellow 2R paste and<br>3.3% Azonine Direct Blue B paste. |
| Dark Bluish-Gray | 6.0% Azonine Direct Blue B paste and<br>0.7% Azonine Direct Red G paste. |

When applied by Methods No. 79 and No. 80 these dyes level well and give colors of very good fastness to rubbing, washing and light. As they do not appreciably stain cotton, they may readily be used in obtaining two color effects on unions containing acetate silk and cotton. Good bright shades are obtained

with 6 to 7.5 per cent of Azonine Direct Yellow 2R paste, Azonine Direct Red G paste, Azonine Direct Blue B paste, or a good black with 2 per cent Azonine SF diazotized and developed with Developer ON. Table LV gives a few formulas for compound shades. Azonine Direct Yellow 2R is probably an aminoazo derivative, perhaps the same as the "Yellow R Paste for Acetate Silk" of Badische.

### *The "Extra Pastes for Acetate Silk"*

The Badische Company now offer a line of dispersol dyes for acetate silk under the above name. The following are available: Yellow 3G Paste for Acetate Silk, Yellow R Paste for Acetate Silk, Yellow RR Paste for Acetate Silk, Orange Extra Paste for Acetate Silk, Pink R Extra Paste for Acetate Silk, Pink B Extra Paste for Acetate Silk, Red R Paste for Acetate Silk, Red Violet Extra Paste for Acetate Silk, Violet B Extra Paste for Acetate Silk, and Blue Extra Paste for Acetate Silk.

At the present time the constitution of these products is not generally known, but the Yellow 3G Paste may be a derivative of nitroaniline; Yellow R Paste an aminoazo derivative; and Orange Extra Paste, Rose R Paste, Red-Violet Extra Paste, and Blue Extra Paste aminoanthraquinone derivatives. This, together with the method of application indicates that they are really dispersol products. It is not known whether they are related to British Patent No. 204,280, of the same company or not. When applied to acetate silk unions in light shades, the cotton usually remains unstained, but heavier dyeings generally tint the cotton somewhat. Yellow R Paste for Acetate Silk is only recommended for self-shades; for compound shades Yellow 3G or Yellow RR Pastes for Acetate Silk should be used.

*Method No. 81: "Extra Pastes" on Acetate Silk.* The paste is first diluted with water at the ordinary temperature and mixed well. This is sieved into a dye bath containing about 2 or 3 grams per liter of green olive oil soap, depending upon the depth of shade, or an equivalent amount of Turkey-red oil, Brilliant Monopole oil, or a similar preparation. For light or medium shades, enter the goods into the lukewarm dye bath and dye for a half

to one hour at 50 to 70° C. (122 to 158° F.). Darker shades may be entered at a higher temperature. The dyed material should be rinsed and brightened in a cold formic or acetic acid bath. The same method is used for piece dyeing.

### *The Cibacete Dyes*

The Cibacete dyes of the Ciba Company, while not in the usual dispersol paste form, are applied by the dispersol method and undoubtedly belong to this general classification. They are in powder form and of exceptionally high tinctorial power, one to two per cent of the dyestuff giving good medium heavy shades. They have good fastness to washing and light, and are applied by the usual simple dispersol process. They leave cotton and the older rayons unstained in most instances but Cibacete Scarlet G stains cotton more than the other members of the group.

The Cibacete dyes are prepared for the dye bath by emulsifying them with sodium or ammonium sulforicinoleate or soap. If hard water must be used in the dye bath, soluble oil should be substituted as the emulsifying agent. The quantity of emulsifying agent to be used depends entirely upon the volume of the dye bath. In general, 2 to 4 grams per liter of dye bath is used. This is dissolved in about 20 times its weight of water at 50 or 60° C. (122 or 140° F.) and the dyestuff added. The mixture is stirred vigorously until solution is complete and then screened into the dye bath. The dyeing is usually complete in about 45 minutes at 20 to 75° C. (68 to 167° F.), when the shade can be brightened with acetic acid.

### *The Cellacete Dyes*

The Cellacete dyes of Kalle are paste products which are merely diluted with hot water for use. They appear to be dispersol products and are applied in a mildly alkaline soap bath. Some members of the group, for instance Cellacete Yellow G and R, may be developed with *B*-naphthol or diamines to give scarlet or bordeaux shades, and Cellacete Orange R gives a deep violet to black shades on development. The present members of the group are: Cellacete Blue F, Cellacete Orange G, 2G, and R, Cellacete Red G,

Cellacete Rose R, Cellacete Yellow G, 5G, 6G, and R. As a class the fastness of the resulting colors to water and washing is satisfactory. The light fastness varies somewhat between the various members of the group, but on the whole is satisfactory.

## *Celanthrene Dyes*

The Newport Chemical Works are preparing a line of Celanthrene dyes for acetate silk[3] which will probably include the following when complete:

| | |
|---|---|
| Celanthrene Blue | Celanthrene Fast Light Yellow |
| Celanthrene Violet B | Celanthrene Yellow |
| Celanthrene Red Violet | Celanthrene Gold Orange |
| Celanthrene Brilliant Red | Celanthrene Fast Light Brown |
| Celanthrene Red B | Celanthrene Black |

The Celanthrene dyes are prepared paste dispersions of anthraquinone derivatives and correspond closely to the Celatene dyes of Scottish Dyes. They are, of course, primarily intended for the dyeing of acetate silk and as a class do not stain cotton. They are not recommended for dyeing unions of wool or true silk with acetate silk, as they stain both true silk and wool. However, the staining of these animal fibers appears to be largely due to a mechanical absorption of the dyestuff, as the colors obtained are not fast to washing. On acetate silk they have excellent general fastness properties and can be used in connection with vat dyestuffs to produce two colored effects on cotton-acetate silk unions. Their fastness to light is of particular interest in this connection. They are readily applied by the usual methods for dispersol products.

The goods should be wet out with Isomerpin or some other suitable reagent in aqueous solution, and then entered into a warm 20 or 40 to 1 dye bath. This bath may be cloudy at the start but gradually clears as the dyestuff is taken up by the fiber. The temperature is gradually raised, during about 30 minutes, to 77 or 82° C. (170 or 180° F.). The dyeing is continued at this temperature until the desired shade is obtained or the bath is fairly well exhausted. This usually requires 30 to 45 minutes longer, and an addition of Glauber's salt may be made to aid the exhaustion. After the dyeing the material is lifted, rinsed, and dried in the

usual manner. For very dark shades a standing bath may be an advantage, in which case an addition of about 70 per cent of dyestuff is made to replenish the bath. While the Celanthrene dyes can be combined with each other to give a wide variety of combination shades, in the application of these combination shades it is advisable to start the dyeing at a temperature below 49° C. (120° F.).

The fastest member of the series is Celanthrene Red Violet. Next in line are Celanthrene Fast Light Yellow and Celanthrene Fast Light Brown. The Celanthrene Violets compare favorably with the various types of vat violets on the market, with which they are probably closely related. The remaining members of the series all have very good fastness to light. Celanthrene Yellow and Celanthrene Black are the poorest members of the class but still show quite good fastness.

### *Newport Dyes*

Among other products which may be applied to acetate silk by the dispersol method may be mentioned Newport Azo Sudan, Azo Yellow B, Azo Orange, Azo Red, and Azo Blue. It is only necessary to dissolve these water-insoluble products in Turkey-red oil, or other suitable, water-soluble solvent, and add this solution to the dye bath. When Turkey-red oil is used as the solvent, the dispersol dyestuff is applied in a soapy dye bath in about the same manner as the S. R. A. dyes. Azo Sudan, Azo Yellow B, and Azo Orange give shades of excellent strength and brilliancy but have a certain tendency to crock. However, this crocking may be entirely remedied by working the dyed acetate silk in a cold bath containing 2 per cent of sodium hydroxide, on the weight of the goods, for 20 minutes. This treatment does not seriously weaken the shades but no doubt saponifies the acetate silk to some extent. Azo Red and Azo Blue do not crock and therefore this severe after-treatment is unnecessary. These colors are only moderately fast to light but wash well.

A number of the Anthrene, as well as other water insoluble vat dyes of suitable constitution may also be applied to acetate silk by the dispersol method, after dissolving the dyestuff in sulfonated

oil or other suitable medium for dispersion. Indigo as well as some of its compounds in the unreduced state have been obtained in the colloidal condition by means of the dispersol process, but most of them have only a very slight affinity for acetate silk. This is particularly true of indigo itself.

*Increasing the Light Fastness of Colors on Acetate Silk*

The fastness to light[2] of many of the more or less light fugitive colors on acetate silk may be very considerably improved by the presence on the fiber of certain colorless organic compounds of a basic nature, such as aniline, *B*-naphthylamine, benzidine, etc. Certain dialkylanilines, such as dimethylaniline, are particularly effective. These products are applied by the dispersol method, that is, they are dissolved in a dispersing agent, such as sulforicinoleic acid or Turkey-red oil, and this is either added to the dispersol dye bath, or applied in a subsequent bath.

Apparently as much as about 2 per cent of the dialkylaniline is taken up by the silk, either in solid solution or chemical combination, due to its high affinity for such basic compounds. As much as 5 per cent of the product appears to have been used in some instances. Where it is all combined in the acetate silk fiber, there is no noticeable odor, but the odor of an excess may be detected. This would apparently indicate a chemical combination with the acetate silk of that portion taken up by the fiber. Their protective action is probably based upon their absorption of the ultra-violet rays as spectroscopic investigation shows that after this treatment, the acetate silk absorbs all light rays below about 3400 A. U. The dialkylanilines are readily prepared for use by the dispersol method by boiling them with about their own weight of Turkey-red oil. This solution is added directly to the aqueous bath.

This process is covered by British Patent No. 243,841 of 1924 to G. H. Ellis and the British Celanese, Ltd., which states that the poor light-fastness properties of the colors given by certain dyes on acetate silk, and even those of good light fastness, may be improved by treating the dyed material with one or more simple amino or substituted amino compounds, such as aniline, alky-

lanilines and alkylphenylenediamines, for example tetraethylphenylenediamines. The effectiveness of the treatment increases with increased alkylation of the treating compound. The amino compounds may be applied in aqueous solution in the form of the free base in any suitable media; as the hydrochloride or other soluble salt; or they may be solubilized or dispersed by suitable solubilizing agents such as those covered by patents No. 219,349, No. 224,925, No. 242,393, or No. 242,711. It is preferred not to use amines which are susceptible to air oxidation, such as diphenylamine, *p*-aminophenol, and *p*-phenylenediamine. The process is more effective upon the azo dyes than with those of any other class.

As an example, 100 pounds of acetate silk may be dyed in any suitable manner with an aqueous hydrochloric acid solution of benzeneazo-*a*-naphthylamine. Then 3 pounds of diethylaniline hydrochloride are dissolved in water and added to a fresh aqueous bath, and the dyed material worked in it until no more amine is absorbed. The resulting shade has a greatly increased fastness to light.

*References*

[1] P. Castan, *Arch. sci. phys. nat. (5), 7,* 196-204 (1925).
[2] G. H. Ellis, *J. Soc. Dyers and Colourists 41,* 98-9 (1925); and *J. Soc. Dyers and Colourists 42,* 184-6 (1926).
[3] P. H. Stott, *American Dyestuff Reporter 16,* 21 (1927).

# CHAPTER XXIII

## THE PATENTS COVERING THE PREPARATION AND APPLICATION OF THE DISPERSOL DYES TO ACETATE SILK AND OTHER FIBERS

WHILE the dispersol dyes are comparatively new products, the first patent covering them having been granted on December 21, 1922, there is at present a rather large number of patents covering their preparation and application. This merely indicates the amount of research that is being done on this one phase of acetate silk dyeing, which in turn emphasizes the growing importance of the whole acetate silk industry.

The following abstracts from the patent literature covering the dispersol dyes are of interest in that they give more definite information than is available from any other source, as to the compounds used in, and the constitution of, the dispersol dyes, as well as the methods of manufacture and application. The patents are given in their numerical order, which appears to be some index as to the sequence of applications. Apparently the first patent on this subject is British Patent No. 207,711.

British Patent No. 207,711, December 21, 1922, to the British Dyestuffs Corporation, J. Baddiley, and W. W. Tatum, covers the use of anthraquinone dyes containing carboxylic groups but no sulfonic groups, on acetate silk. Suitable dyes are those obtained by condensing salicylic acid *p*-sulfonyl chloride with diaminoanthraquinones, as described in British Patent No. 201,610, or by condensing haloanthraquinones with a suitable aminocarboxylic acid, such as anthranilic acid. The dyeing is effected in a neutral or slightly alkaline bath, with a subsequent addition of salt or acid to aid exhaustion. These products give blue shades which are unobtainable with azo compounds, and they have the excellent fastness to light and washing common to the anthraquinone dyestuffs. In this manner 1,5-dichloroanthraquinone with anthranilic acid dyes acetate silk directly a reddish-violet shade (Duranol

Violet 2R?). 4-Brom-1-methylaminoanthraquinone with anthranilic acid gives direct reddish-blue shades, while dichloroanthrarufin with anthranilic acid gives greenish-blue shades (Duranol Blue G?). 1,4-Diaminoanthrarufin, and diaminoanthrarufin with the *p*-sulfonyl chloride of salicylic acid, and the dinitro-1, 5-dichloroanthraquinone and anthranilic acid are also mentioned. The latter product is reduced. Undoubtedly this patent covers some of the Duranol dyes and probably some of the Celatenes. Also see British Patents No. 225,678 and No. 227,923, and United States Patent No. 1,574,748.

From the above there does not appear to be any reason why these products could not be applied by the usual "direct" method used for applying the acid and mordant type of dyes to acetate silk. However, as might be expected, these anthraquinone compounds are not very soluble in water, although they are not exactly insoluble. For this reason they are well adapted for application by the dispersol method, where their slight solubility in water allows them to react readily with the fiber and the large surface of the dispersol dyestuff phase allows a very rapid renewal of the dyestuff removed from solution by the fiber. Then too their comparatively slight solubility in water is a factor in favor of dyeing acetate silk.[a]

British Patent No. 201,610, April 28, 1922, to the British Dyestuffs Corporation, J. Baddiley, and W. W. Tatum, which is mentioned in the above patent No. 207,711, and also in No. 225,678, covers acid and acid-mordant wool dyes of the anthraquinone series, some of which may also have an affinity for acetate silk. This patent states that wool dyes of excellent fastness to milling and washing are obtained by condensing the amino derivatives of anthraquinone with the sulfochlorides of salicylic acid, either with or without a condensing agent. For example: a blue dyestuff is produced by heating a mixture of 27 parts of tetraaminoanthraquinone, 25 parts of salicylic sulfochloride, 17 parts of fused sodium acetate, and 210 parts of nitrobenzene at 135° C. for 3 hours, freeing the product from nitrobenzene by steam distillation and precipitating the dyestuff with salt.

[a]See Chapter VIII.

British Patent No. 203,051, May 31, 1922, to Imray, for the Ciba Company, and United States Patent No. 1,586,911, to W. Moser (June 1, 1926), assigned to the same company, covers the preparation of 2,3-diaminoanthraquinone from 2-amino-3-bromoanthraquinone by heating it with ammonia, or a liquid containing ammonia, in a closed vessel at 170 to 190° C., with or without the addition of a catalyst. The product dyes acetate silk a pale yellowish-brown color.

According to British Patent No. 211,720 to the British Dyestuffs Corporation, J. Baddiley, and A. Sheperdson, March 8, 1923, acetate silk may be dyed yellow to blue shades in an aqueous dye bath containing aminoanthraquinone dyes in colloidal solution or suspension. The presence of emulsifying agents, such a Turkey-red oil, in the dye bath is advantageous. In this manner 1-aminoanthraquinone gives a yellow shade; 1-amino-2-methylanthraquinone gives a yellowish-orange; 1-methylaminoanthraquinone a red; 1, 4-diaminoanthraquinone a violet; 1, 5-diaminoanthraquinone a red; diaminoanthrarufin a blue; 1,4-aminohydroxyanthraquinone a crimson; and diaminoanthrarufin, when methylated in one or both of the hydroxy groups, a sky blue shade.

F. Bayer & Company in British Patent No. 214,246, April 14, 1923, cover the dyeing of acetate silk with solutions prepared by dissolving unsulfonated dye bases of the triphenylmethane, anthraquinone, or other series in glycerol, epichlorohydrin, ethylene chlorohydrin, or other organic solvent and diluting this solution with water to obtain the base in a finely divided state. Its colliodal condition may be improved by adding glue, gelatin, or Turkey-red oil to the bath. For instance: Methyl Violet 6B base, China Green base (*p, p′*-tetramethyldiaminotriphenylcarbinol anhydride), or Alizarin Geranol base, can be dissolved in ethylene chlorohydrin, diluted with water, glue or Turkey-red oil added, and the acetate silk dyed at 50 to 60° C. (122 to 140° F.).

The British Patent No. 214,765, February 8, 1923, to H. A. E. Drescher, J. Thomas, and Scottish Dyes, states that anthraquinoneimides of dibasic acids are obtained by heating a halogenanthraquinone with an imide of a dibasic acid in the presence of copper and an acid absorber, or with copper and a metal imide salt.

The imides yield aminoanthraquinones upon hydrolysis, as for instance with sulfuric acid. It describes the preparation of numerous compounds, including 1-phthalimidoanthraquinone, 1, 5-diphthalimido-, 1, 5-diamino-, 1-chloro-5-phthalimino-, and 1-chloro-5-aminoanthraquinones, 4-phthalimido and 4-amino-1-methylamino-2-bromoanthraquinone, 1-phthalimido-2-nitro- and 1-amino-2-nitroanthraquinones. This patent is mentioned in connection with British Patents No. 230,116 and No. 231,206, etc., which cover dispersol products; and United States Patent No. 1,528,470 covers the preparation of the compounds mentioned.

British Patent No. 219,349, January 27, March 17, and May 22, 1923, to British Celanese, Ltd., formerly the British Cellulose and Chemical Manufacturing Company, and G. H. Ellis gives considerable detail regarding the dispersol dyes, and as this company manufactures the S.R.A. dyes, we may assume that it very largely covers these products. According to this patent, dyes which are capable of coloring acetate silk, but which are too insoluble in water to be applied by the usual methods, may be treated with the higher fatty acids, or their derivatives which contain salt-forming groups, such as sulforicinoleic, oleic, stearic or palmitic acid, or their alkali or ammonium salts, to form colloidal solutions or dispersions and thus become sufficiently soluble or dispersed to allow their use in the commercial dyeing of acetate silk in aqueous dye baths.

A wide range of insoluble products may be applied by this method. The simple aromatic amino bases may be applied in this manner for the production of insoluble azo colors on the fiber, and they may be used either in the impregnating or developing bath or in both. Many unsulfonated azo dyes, unreduced dyestuffs of the Indophenol and Indigoid classes, basic derivatives of the anthraquinone series, and the color bases of diphenylmethane, triarylmethane, oxazine, azine, and thiazine dyes may be also be dispersed by this method. In general, most of the dyes or compounds must be in the form of free bases, and should contain no sulfonated groups for the reasons previously given. Other substituent groups, such as primary, secondary, and tertiary amino groups, nitro, nitroso, hydroxy, methoxy, or halogen groups, may be present and

where a free primary aromatic amino group is present, it may be diazotized and developed on the fiber by the methods given under the Developed Colors, Chapters XVI and XVII.

To prepare the soluble product, the dyestuff or other organic compound to be used, is mixed, with or without heat, with the free fatty acid, or its alkali or ammonium salt, the resulting mixture being subsequently diluted with water or a solution of alkali, boiled, and filtered through cloth into the dye bath, which may be either neutral, acid, or alkaline. If desired, suitable dyeing materials may be converted into "solid solutions" or complexes by heating them with the appropriate oily body followed by the requisite treatment to render them fit for transport.

Dyes dispersed in this way may be used, with or without the addition of other dyestuffs not deleteriously affected by the solubilizing agents, for dyeing, printing, or stencilling fabrics containing acetate silk in unions with other fibers or threads, the nonsulfonated azo dyes being preferentially fixed by the acetate silk, leaving the cotton, wool, silk and regenerated rayons unstained or but slightly stained. These latter fibers may be subsequently or simultaneously dyed with suitable dyestuffs which have no affinity for the acetate silk. The Indophenol type of dyes are very suitable for blue and violet shades. Benzeneazobenzeneazo-*B*-naphthol (Sudan III), 4-nitro-2-methoxybenzene-1-azodiphenylamine, and aminoazonaphthalene are also mentioned.

For example, pink and red shades may be obtained on acetate silk by treating 4-nitro-2-methoxybenzene-1-azodimethylaniline with sufficient oleic acid to dissolve it on heating, and then pouring the hot solution into hot water containing enough ammonia or sodium carbonate to neutralize the fatty acid. This mass is filtered into the dye bath.

An orange shade on 100 kilos of acetate silk may be obtained by heating a kilo of finely ground *p*-nitrobenzeneazodiphenylamine with 10 liters of 50 per cent sodium sulforicinoleate. This is diluted with boiling water and boiled, after which it is added to the 30 to 1 dye bath and the yarn dyed in the usual manner, raising the temperature to 65 to 75° C. (147 to 167° F.) if necessary.

A scarlet shade on the same quantity of acetate silk may be obtained with 1.5 kilos of aminoazobenzene and 15 liters of 50

per cent sodium sulforicinoleate. After dyeing, rinse the stock and diazotize. Then rinse again and develop in a solution containing 3 kilos of dimethylaniline in 20 liters of 50 per cent sodium sulforicinoleate, prepared in the same manner as the red dye above.

In a somewhat similar manner 25 kilos of a 50-50 acetate silk-cotton union fabric may be dyed, the acetate silk a bluish-red and the cotton a blue shade. Heat 250 grams of finely powdered 2, 4-dinitrobenzene-1-azodiethylaniline for 10 minutes at 100° C. (212° F.) in 5 liters of 50 per cent sodium sulforicinoleate. This dispersol dye compound is diluted with boiling water, boiled, filtered into a 750 liter dye bath, and the union entered. When the acetate silk has reached the desired shade, the material is removed from the bath, rinsed in warm water and the cotton dyed a blue shade in a dye bath containing 375 grams of Chlorazol Fast Blue 2B. Possibly Diamine Fast Blue FFB, Direct Fast Blue FF or Solamine Blue FF could also be used for the cotton.

The Indophenols may be applied by first converting them into water-soluble bodies by treatment with fatty or sulfonated acids giving water soluble sodium or ammonium salts, such as sulforicinoleic acid. Glue may also be used. For instance, 500 grams of diethyl-*p*-aminophenol-1,4-naphthoquinonemonoimide may be ground with 10 liters of water and this added to 2000 liters of water containing 4 kilos of glue. The dyeing is carried out at 40 to 70° C. (104 to 158° F.). The glue may be omitted if the dyestuff is first dissolved in a suitable solvent and poured into water to obtain a fine suspension.

In British Patent No. 222,001, November 27, 1923, to A. J. Hall and Silver Springs Bleaching and Dyeing Company, it is stated that acetate silk may be dyed yellow to red shades of excellent fastness, especially to washing, light and chlorine, by means of 2, 4-dinitrochlorobenzene derivatives, produced by condensing 2, 4-dichlorobenzene with aromatic compounds containing one or more amino groups, but no sulfonic acid groups. For instance 2, 4-dinitrodiphenylamine and its 2′- or 4′-hydroxy- derivative, 2, 4-dinitro-2′-hydroxydiphenylamine, or 2, 4-dinitro-4′-hydroxydiphenylamine; the carboxyl derivatives 2, 4-dinitro-2′-carboxyldiphenylamine; and 2, 4-dinitro-4′-carboxyldiphenylamine; 2, 4-dinitro-4′-aminodi-

phenylamine, 2, 4-dinitro-4′-acetylaminodiphenylamine, and 2, 4-dinitro-*N*-methyldiphenylamine, may be used for dyeing acetate silk directly from a solution or dispersion in water at 75° C. (167° F.). Turkey-red oil, soap, or ammonia may be added to the bath. Cotton or artificial silk are not stained.

In British Patent No. 224,077, October 19, 1923, and United States Patent No. 1,534,019, April 21, 1925, to the British Dyestuffs Corporation, Baddiley, Hill, Lawrie, Shepherdson, and Swann, it is proposed to disperse water-insoluble, or nearly insoluble dyes, which have an affinity for acetate silk, in the condensation products of naphthalene or naphthalenesulfonic acids with formaldehyde. Dyes such as those specified in British Patent No. 211,720 are suitable and such dispersing agents may be used to dye acetate silk a yellowish-red with the monoazo dye prepared from diazotized *p*-nitroaniline and diphenylamine; or violet-red with a dispersion of 1, 4-diaminoanthraquinone. These products may be mixed with direct cotton dyes for use on unoins, etc. Also see British Patent No. 246,984. Pastes containing these protective colloids and suitable dyes may be evaporated to dryness and ground to a powder for shipment or storage.

Excellent black shades on acetate silk may be obtained without double diazotization and double coupling by the method covered in British Patent No. 224,359 of 1923 to Lawrie, Blackshaw, and the British Dyestuffs Corporation. In this process bases such as *a*-naphthylamine, benzidine, toluidine and *p, p′*-diaminodiphenylamine are applied to the fiber in the free condition, or are produced on the fiber in this state by known methods, *e.g.*, hot dispersions in such liquids as aqueous alcohol or Turkey-red oil. A "basic" salt of the base may be used and the base subsequently liberated on the fiber by means of sodium carbonate. It can then be diazotized and developed with *B*-hydroxynaphthoic acid or resorcinol in a slightly acid bath. The fact that reddish azo dyes are ultimately obtained from the same base when they are applied in the ordinary manner, that is, without the liberation of free base, is said to be due to the small amount of dyestuff on the fiber, whereas by this process a much larger quantity of the base and consequently a correspondingly larger amount of dyestuff is present on the acetate silk.

In British Patent No. 224,681, October 11, 1923, to British Celanese, Ltd., Ellis, Stevenson, and Croft, it is stated that acetate silk may be dyed, printed or stencilled by means of non-sulfonated pyrazolone compounds, particularly the non-sulfonated azo derivatives. For instance, azo dyes prepared by coupling unsulfonated diazo compounds with 1-phenyl-3-methyl-5-pyrazolone, benzene-azo-1-phenyl-3-methyl-5-pyrazolone, 1,3-dimethyl-5-pyrazolone, *p*-methoxybenzeneazo-1-phenyl-3-methyl-5-pyrazolone and dimethyl-*p*-aminobenzeneazobenzeneazo-1-phenyl-3-methyl-5-pyrazolone. The dyes may be used in solution with sodium hydroxide, or dissolved in an organic solvent miscible with water and then mixed with water, or may be dispersed in sulforicinoleic acid or other solubilizing or dispersing agents, as described in British Patent No. 219,349. These dyes may be used in conjunction with others for dyeing mixed goods containing acetate silk together with cotton, silk, or wool, usually giving yellow to orange shades. United States Patent No. 1,600,277, September 1, 1926, to Ellis, Stevenson and Croft; and Canadian Patent No. 260,530, May 4, 1926, to the same inventors, cover this process.

In British Patent No. 224,925, May 22, 1923, to Ellis and the British Cellulose and Chemical Manufacturing Company, they state that it is of some advantage to substitute carbocyclic compounds containing salt-forming groups for the sulforicinoleic acid compounds specified in British Patent No. 219,349, as the solvent or dispersing agent. Suitable compounds are given as naphthenic acids and naphthalenesulfonic acid or other carboxylic or sulfonic acids of the cycloparaffins or phenols; and the sulfonic, carboxylic, and phenolsulfonic acid derivatives of the benzene, naphthalene, or anthracene series. In certain cases it may be of advantage to use the above in combination with the older reagent; *i.e.*, sulforicinoleic acid. For example, one pound of *m*-nitrobenzeneazodiphenylamine is finely ground and heated with 9 pounds of naphthenic acid until homogenous, sufficient sodium hydroxide being then added to give the product a slightly alkaline solution. After filtration, this is suitable for direct addition to the acetate-silk dye bath. A blue is obtained in a similar manner with 1-methylamino-4-*p*-tolylamino-anthraquinone. Also see German Patent No. 303,121 and United States Patent No. 1,610,961.

British Patent No. 225,678, October 23, 1923, another addition to British Patent No. 201,610, and to the same inventor, describes the manufacture of other acetate silk dyes by substituting the sulfochlorides of other *o*-hydroxycarboxylic acids, such as *o*-cresotic acid, for the salicylic sulfochlorides of the principal patent. For instance, ten parts of 1, 4-diaminoanthraquinone, either dissolved or suspended in 60 parts of acetic acid are stirred with 12 parts of *o*-cresotic sulfochloride at 60° C. for 4 hours, during which time 4 parts of anhydrous sodium acetate are gradually added. After the separation of the dye, it is converted into its sodium salt, the solution filtered from the uncondensed diamine, and the dyestuff salted out. This product dyes wool a bluish-red shade and has a high affinity for acetate silk (Duranol Red 2B?). Also see British Patent No. 207,711.

British Patent No. 227,183, October 19, 1923, addition of British Patent No. 219,349, to Ellis and the British Cellulose and Chemical Manufacturing Company, covers the use of vat dyes of the anthraquinone class, such as Indanthrene, Cibanone, Algol, etc., stabilized as in the main patent. For example, one pound of Algol Pink R (1-benzoylamino-4-hydroxyanthraquinone) is made into a paste with 9 or 10 pounds of 50 per cent sodium Turkey-red oil previously heated to 90° C. (194° F.) and the heating continued until the dye is dissolved. This paste is diluted with a boiling 3 to 5 per cent solution of neutral soap, and the mixture added to the 300 to 500 gallon dye bath. The above is sufficient to dye 100 pounds of acetate silk, after which it is rinsed, dried, etc. It is possible that many other vat dyes may be applicable by the same process, as for instance, Indanthrene X (*N*-dihydro-1, 2, 1′, 2′-anthraquinoneazine), Indanthrene Bordeaux B (6, 6-dichloro-2, 7-di-*a*-anthraquinonyldiaminoanthraquinone), Algol Rose B (1-benzoylamino-4-methoxyanthraquinone), Algol Scarlet G, Algol Yellow WG (1-benzoylaminoanthraquinone), Algol Violet B (1-benzoylamino-4, 5, 8-trihydroxyanthraquinone), etc.

British Patent No. 227,923, October 25, 1923, to the British Dyestuffs Corporation, J. Baddiley and W. W. Tatum, states that acid dyestuffs having an affinity for acetate silk may be prepared by condensing the 1, 5-dichloro- derivatives of anthraqui-

none, such as 4, 8-dinitro-1, 5-dichloroanthraquinone, with 2 molecules of anthranilic acid, and reducing. The value of these dyes is enhanced when they contain amino or hydroxy groups in the *p*-position to the aminobenzoic residue. For instance, 4, 8-diphenylaminoanthrarufin-*o, o'*-dicarboxylic acid (from 4, 8-dichloroanthrarufin) dyes acetate silk a greenish-blue (Duranol Blue G ?) ; and 4, 8-diphenylamino-1, 5-diaminoanthraquinone-*o, o'*-dicarboxylic acid (from 1, 5-dichloro-4, 8-dinitroanthraquinone, the nitro group being reduced with sodium sulfide after condensation) dyes acetate silk a green color.

British Patent No. 230,116, September 3, 1923, to Scottish Dyes, E. G. Beckett, and J. Thomas, covers the production of a purple dye for acetate silk from phthalimidoanthraquinone, described in British Patent No. 214,765. The nitration of 1-phthalimidoanthraquinone at 15 to 20° C. (57 to 66° F.) in concentrated sulfuric acid gives a dinitro derivative which is hydrolyzed by 85 per cent sulfuric acid at 85° C. (185° F.) to a dinitro-1-aminoanthraquinone. This upon reduction with soduim sulfide in an aqueous sodium hydroxide solution at 80° C. (176° F.) gives triaminoanthraquinone, bronze crystals which in aqueous suspension dye acetate silk deep purple shades. The triaminoanthraquinone may be benzoylated with benzoyl chloride in pyridine or nitrobenzene solution to give a reddish-purple crystalline product which dyes cotton bluish-red shades fast to washing, bleaching, and light, from an alkaline hydrosulfite vat. Possibly the above patent may cover Celatene Brilliant Violet B.

British Patent No. 231,206, March 21 and September 14, 1923, to Scottish Dyes, E. G. Beckett, J. Thomas, and J. Tonkin, states that acetate silk is dyed greenish-blue to deep blue shades by immersion in a hot aqueous suspension of hexa-aminodianthraquinonylthioether, or a dyestuff obtained by the nitration of 1, 5- or 1, 8-diphthalimidoanthraquinone (see British Patent No. 214,765) and subsequent hydrolysis of the product by means of an alkaline sulfide. For example, a blue dyestuff is obtained by nitrating 50 grams of 1, 5-diphthaliminoanthraquinone, dissolved in 500 grams of 97 per cent sulfuric acid, for an hour at 30° C. (87° F.) by the addition of 62 grams of 80 per cent nitric acid and 50 grams of

97 per cent sulfuric acid. The product is poured into 5 liters of water, filtered, the residue washed free from acid, heated for one hour at 80° C. (176° F.) in 1500 cubic centimeters of water containing 227 grams of sodium sulfide crystals and 35 grams of sodium hydroxide, the product hot filtered, and the dyestuff residue washed and dried. The resulting blue dye is slightly soluble in water and may correspond to Celatene Blue. Also see British Patent No. 253,584.

British Patent No. 233,813, February 27 and November 22, 1924, to the British Dyestuffs Corporation, J. Baddiley, and H. Browning, Jr., given in connection with the vat dyes, covers the dyeing of acetate silk by means of aqueous suspensions of vat dyes, as well as certain indophenols.

According to British Patent No. 234,533, January 26, 1924, to Scottish Dyes, J. Thomas, and L. J. Hooley, hydroxyanthraquinone and their chloro derivatives suitable for dyeing acetate silk may be prepared by the condensation of phthalic anhydride with *o*-chlorophenol or its derivatives, such as 2, 4-dichlorophenol in sulfuric acid solution in the presence of boric acid. The hydroxyanthraquinone derivatives are separated by the action of alkalies. For example, chloroquinizarin may be prepared by slowly adding 20 parts of 2, 4-dichlorophenol to 65 parts of 20 per cent oleum while stirring and cooling to hold the temperature below 25° C. (77° F.). When a test sample of this is soluble in a 12 per cent sodium chloride solution, 22 parts of phthalic anhydride, 10 parts of boric acid and 30 parts of 20 per cent oleum are added, and the temperature raised to 180° C. in the course of about three hours. It is then raised to about 200° C. in an hour and held at 195 to 200° C. for about 6 hours. The solution is then diluted with water and the precipitate extracted with dilute alkali, whereby an insoluble substance which appears to be 1, 4-dihydroxy-2-chloroanthraquinone is obtained as residue. The soluble portion dyes acetate silk a red shade and wool in reddish shades which become bluer on chroming. This may cover Celantene Red B.

In another example, a mixture of 150 parts by weight of 94 per cent sulfuric acid, 30 parts of phthalic anhydride, 16 parts of *o*-chlorophenol and 16 parts of boric acid, is heated to 180° C. for

3 hours, the temperature is raised to 200° C. for an hour and then maintained at 195 to 200° C. for 6 hours. After cooling, boiling with 3000 parts of water, and filtering, a quantity of the residual paste equivalent to 10 parts of dry material is boiled with 1000 parts of water and 32 parts of ammonia. The insoluble portion is filtered off, and the soluble portion, consisting mainly of 2, 3-chlorohydroanthraquinone, is precipitated by acidification. The portion insoluble in ammonia gives fast orange-yellow shades on acetate silk. This may be either Celatene Yellow, Orange, or Golden Orange.

Fast greenish-yellow shades on acetate silk, which are not phototropic, may be obtained by means of monoazo dyestuffs prepared by coupling 1, 3-dihydroxyquinoline with diazotized aniline or its homologues or derivatives, as described in British Patent No. 11,205 of 1905. This process is covered by British Patent No. 236,037, June 20, 1924, to Baddiley, Hill, and the British Dyestuffs Corporation. Possibly this patent may cover Dispersol Yellow 3G, the exact composition of which is not commonly known at present.

British Celanese Ltd., in British Patent No. 237,943, April 4, 1924, states that unsulfonated nitro derivatives of diarylamines which may or may not contain hydroxyl, amino, or chloro groups, may be applied to acetate silk by the usual dispersol methods of dyeing, printing, or stencilling. They may be dissolved in a sulfonated fatty acid or carboxylic or phenol sulfuric acid, as in British Patent No. 219,349, to give greenish, golden-yellow, orange, and brown shades which are generally of very good fastness to light, soaping, acids, alkalies, and ironing. Suitable derivatives include 2, 4-dinitrodiphenylamine, 2, 4-dinitro-4-hydroxydiphenylamine (see British Patent No. 222,001), 4-chloro-4-nitrodiphenylamine, 4-chloro-2-nitro-4-aminodiphenylamine, 4, 4′-dinitro-2′-hydroxydiphenylamine, 4-nitrophenyl-4′-nitro-2′-tolyulamine, and 2, 4-dinitrophenyl-*B*-naphthylamine. Such compounds usually have no affinity for cotton.

For instance, 100 pounds of acetate silk may be dyed a full gold shade as follows: Heat 5 pounds of a 20 per cent aqueous paste of 2, 4-dinitro-4-hydroxydiphenylamine with 7.5 pounds of

65 per cent aqueous ammonium sulforicinoleate until the mass is homogeneous. Then dilute this with boiling water to make 12 gallons and sieve it into a 200-gallon dye bath. The wet-out acetate silk is then entered and dyed at 65 to 75° C. (149 to 167° F.).

Another patent covering the dispersol products is British Patent No. 238,936, May 26, 1924, to Scottish Dyes, E. G. Beckett, and J. Thomas. It states that acetate silk may be dyed colors which are fast to light by means of aqueous suspensions or colloidal solutions of derivatives (other than amino derivatives) of *a*-hydroxyanthraquinone, which contain at least one other hydroxyl or halogen substituent in the molecule, but not those polyhydroxyanthraquinones which contain two hydroxyl groups in the ortho position to one another. Suitable dyes are 1, 5-dihydroxyanthraquinone (yellow), 1-hydroxy-4-chloroanthraquinone (yellow), 1, 6-dihydroxyanthraquinone (yellow), 1, 4-dihydroxyanthraquinone (orange), leuco-1, 4-dihydroxyanthraquinone (reddish-yellow), 1, 4, 6-trihydroxyanthraquinone (reddish-yellow), and 1, 4, 6-trihydroxy-2-chloroanthraquinone (reddish-yellow). These dyes are suitable for use on the acetate silk of acetate silk-cotton unions, since they do not dye cotton. As an example, a lemon yellow color is obtained by working 100 parts of the yarn for an hour at 70° C. (158° F.) in a dye bath containing 10 parts of a 10 per cent paste of 1-hydroxy-4-chloroanthraquinone in suspension in 2000 parts of water. The dyed fabric should be soaped lightly, rinsed, and dried, as usual.

The British Celanese Company and G. H. Ellis obtained British Patent No. 239,470 on April 4, 1924, covering the dyeing, stencilling, or printing of acetate silk by means of aqueous suspensions or colloidal solutions, but not solubilized forms (as in British Patent No. 219,349) of unsulfonated mono-, di-, or poly-nitro derivatives of diarylamines, but excluding 2, 4-dinitrodiarylamines (see British Patents No. 237,943 and No. 222,001), which may or may not contain hydroxy, chloro, amino, or other substituent groups. Such substances have practically no affinity for cotton, and only a slight affinity for silk and wool. These are either insoluble or only slightly soluble in water, dilute acids, or alkalies, and are applied in the form of fine suspensions, to which may be added protective

colloids, such as glue, starch, or gums. They yield greenish-yellow to brown shades on acetate silk which generally show very good fastness to light, soaping, acid, alkalies, and ironing. Suitable compounds include 4-nitrodiphenylamine, 4-nitrophenyl-4′-tolylamine, 4-chloro-2-nitrodiphenylamine, 4-nitro-4′-chlorodiphenylamine, 4-chloro-2-nitro-4′-methoxydiphenylamine, 4-chloro-2-nitro-4′-hydroxydiphenylamine, 4-chloro-2-nitro-3′-aminodiphenylamine, 4,4′-dinitrodiphenylamine, 4, 4′-dinitro-3′-hydroxydiphenylamine, 4-nitrophenyl-4′-nitro-2′-tolyamine, 2, 4-dinitrodiphenylamine, 4, 4′-dichloro-2-nitrodiphenylamine, and 4, 4′-dinitro-2′-hydroxydiphenylamine.

British Patent No. 242,393, September 19, 1924, an addition to patent No. 219,349, to British Celanese and Ellis covers another dispersing agent for the dispersol dyes mentioned in the original patent, as well as in patents No. 224,681, No. 227,183, and No. 237,943. According to this patent, solubilized dyestuffs suitable for dyeing acetate silk are prepared by treating the insoluble dyes with sulfoaromatic fatty acids; as, for instance, sulfobenzenestearic acid (Twitchell reagent), or their derivatives, such as sulfophenolstearic acid and sulfonaphthalenestearic acid, or their salts, which act as solubilizing agents. A suitable solubilizing agent is prepared by adding a cold paste containing 25 kilograms of naphthalene or benzene and 25 kilograms of oleic acid to 100 kilograms of 20 per cent oleum at 40° C. (104° F.), the temperature being then raised to 100° C. (212° F.) and maintained for 3 hours. The product is poured into 250 liters of water containing 50 kilograms of sodium chloride and the upper layer separated and purified. Also see United States Patent No. 1,610,961.

According to British Patent No. 242,711, August 14, 1924, to British Celanese, G. H. Ellis, and W. O. Goldthorpe, the dyeing, printing, or stencilling of acetate silk with insoluble dyes and fatty substances, such as sodium sulforicinoleate, as described in British Patent No. 219,349, No. 224,681, No. 227,183 and No. 237,943, is aided by the presence of secondary solvents. These secondary solvents may be alkyl or alkylene halides, such as tetrachlorethane and trichlorethylene; simple or mixed cyclic or aromatic derivatives containing one or more amino, chloro, or hydroxy groups,

such as cresols, alkylanilines, toluidines, chlorophenols, and mono- or poly-chlorobenzenes; and hydrogenated derivatives of such or other aromatic compounds; as for instance hexahydrophenol, hexahydrocresols, hexahydrobenzene, decahydronaphthalene and tetrahydronaphthalene. The presence of such solvents results in improved depth of shade, penetration and levelness, and a consequent economy in dyes. The mixture of dye, oil, and solvent may be made in any order, much or little water may be used, and the mixture may be subsequently concentrated or dried before addition to the dye bath or printing paste. Insoluble diazotizable substances may be applied in this way for development on the fiber.

British Patent No. 243,505, July 2, 1924, to J. Thomas and the Scottish Dyes, Ltd., covers the preparation of certain aminoanthraquinone compounds. Nitroanthraquinone derivatives substituted in the *B*-position are produced by condensing benzoylbenzoic acids substituted in the *p*-position in the presence of strong sulfuric acid or weak oleum, and nitrating the anthraquinone derivatives formed by the condensation, without separating them from the solution. The products are subsequently converted into the corresponding amino-compounds and simultaneously purified by treatment with alkaline reducing agents followed by washing with water. For example, a solution of 11.1 parts by weight of *p*-chlorobenzoylbenzoic acid, which is prepared by condensing chlorobenzene with phthalic anhydride in the presence of aluminum chloride, in 55.5 parts of 6 per cent oleum, is maintained at 140° C. for 2 hours, and then cooled below 18° C., when 3.5 parts of sodium nitrate are added during a half-hour, while stirring. After keeping for 16 hours, the melt is boiled with 600 parts of water, and filtered after further dilution with water. A quantity of the moist product containing 10 parts of crude nitro-2-chloroanthraquinone is boiled for an hour with a solution of 25 parts crystalline sodium sulfide in 450 parts of water, and the product is filtered off and washed, yielding 9 parts of amino-2-chloroanthraquinone, melting at 176 to 180° C. Nitro and amino-2-methylanthraquinone are prepared in the same manner from *p*-toluoylbenzoic acid. Also see British Patents No. 228,634, No. 230,130, No. 231,206, No. 238,590 and No. 238,936.

British Patent No. 244,143 to the British Celanese Company, G. H. Ellis, and E. Greenhalgh, covers the printing or stencilling of acetate silk by means of insoluble or relatively insoluble coloring matters, compounds, or components; for example, those referred to in patents No. 219,349, No. 224,681, No. 224,925, No. 227,183 and No. 237,943, solubilized by treatment with the solubilizing agents of patents No. 219,349 and No. 224,925. In this patent it is proposed to add one or more swelling agents having a solvent action towards cellulose acetate to the printing paste. The thiocyanates of alkali metals or of ammonia (particularly for neutral or alkaline preparations), zinc chloride or nitrate, and salts of organic sulfonic acids such as those of benzene, naphthalene, or anthracene, or of their substitution derivatives, for example, naphthol, phenol, or aminonaphthols, are mentioned as suitable products. In an example, a bluish-red shade is obtained on acetate silk by printing on a color paste containing 40 grams of paste prepared from 2, 4-dinitrobenzene-1-azodimethylaniline solubilized by pretreatment with sodium sulforicinoleate, 5 grams of soda ash, 20 grams of ammonium thiocyanate, 40 grams of water and 295 grams of a thickening agent, prepared from British gum and gum arabic. Also see the patents covering the "assistants" used for the basic dyes, the ammonium thiocyanate method of applying basic dyes, and Dyeing by Precipitation, Chapters X and XI.

British Patent No. 244,936, January 24, 1925, to L. B. Holliday and Company, and A. Young, states that acetate silk may be dyed by aqueous solutions or suspensions of the products obtained by condensing 1-chloro-2, 4-dinitrobenzene-6-sulfonic acid or 1-chloro-2, 6-dinitrobenzene-4-sulfonic acid or their salts with aromatic substances containing one or more amino- or one or more hydroxy groups, as for instance aniline. For example, 320 grams of potassium 1-chloro-2, 4-dinitrobenzene-6-sulfonate are boiled with 100 grams of sodium acetate in a liter of water. Ninety-three grams of aniline are then added to the boiling solution, when a bright yellow solid separates almost immediately. When the reaction is complete, the liquor is cooled and the 2,4-dinitrodiphenylamine-6-sulfonic acid collected. The dyeing may be carried out by the immersion of the acetate silk in an aqueous solution or suspension

of the dyestuff and heating to about 75° C. A little ammonia, Turkey-red oil, or soap may be added and the goods are finally soaped, rinsed, and dried.

British Patent No. 246,984, January 7, 1925, an addition to patent No. 224,077, to the British Dyestuffs Corporation, J. Baddiley, A. Shepherdson, H. Swann, J. Hill, and L. G. Lawrie, is an improvement over the original patent, in that it is proposed to use much less dispersing agent in the preparation of the dispersol dye product. For instance, less than 10 per cent, on the weight of dry dyestuff, of the condensation products of napthalene with formaldehyde is used in solubilizing the dye. As an example, a dye paste consists of 10 parts of aminoanthraquinone, 0.25 part of the dispersing agent, and 89.75 parts of water. Further, complete neutralization of the acidic dispersing agent in the solubilized dyestuff paste by the addition of ammonia is preferred to the partial neutralization with sodium hydroxide as mentioned in the chief patent.

British Patent No. 251,155, August 14, 1925, to Johnson for the Badische Company and French Patent No. 600,106, June 26, 1925, to the same company cover the dyeing of acetate silk in fast shades from aqueous solutions or suspensions, with or without dispersing agents, such as Turkey-red oil, of azo dyes containing one or more monohydroxyethylamino groups ($-NH.CH_2.CH_2.OH$) but no sulfonic acid groups. A suitable dye is obtained by coupling diazotized *p*-nitroaniline or *m*-nitro-*p*-toluidine with hydroxyethylaniline in acetic acid solution.

British Patent No. 253,584, March 16, 1925, to Scottish Dyes, Thomas, Beckett, and Tonkin, an addition to Patent No. 231,206, specifies that an alkaline earth sulfide, such as calcium hydrogen sulfide, may be used to advantage in place of the alkali sulfide of the original patent. Thus, in place of 168 parts of sodium sulfide crystals, 73 parts of calcium hydrogen sulfide may be used.

According to British Patent No. 253,978, March 18, 1925, to G. H. Ellis and the British Celanese Company, acetate silk may be dyed, printed or stencilled with dyestuffs of the stilbene group containing no sulfonic groups, either by the dispersol process, as in Patent No. 224,925, or they may be formed within the acetate

silk fiber by coupling the diazotized aminostilbenes with suitable developers. The following are mentioned as suitable dyestuffs: stilbenedisazobisphenol (yellow), stilbenedisazo-*m*-toluidine (gold), stilbenedisazo-*a*-naphthylamine (red), aminostilbeneazo-*m*-phenylenediamine (gold), and aminostilbeneazo-*m*-toluidine (yellow). Diaminostilbene may be applied to acetate silk and then diazotized and coupled with phenol (gold), 1-phenyl-3-methyl-5-pyrazolone (red), diethylaniline (red), *m*-phenylenediamine (reddish-brown), *m*-phenylenediamine (reddish-brown); *a*-naphthylamine (plum), *B*-naphthylamine (plum), or *B*-hydroxynaphthoic acid (black). These dyestuffs have little or no affinity for fibers other than acetate silk.

Also see British Patent No. 255,962 in Chapter XVI.

British Patent No. 256,205 to the Society of Chemical Industry of Basle covers the preparation of monoazo dyestuffs which give a fast yellow color on acetate silk by coupling 1-(2′-chlor)-phenyl-3-methyl-5-pyrazolone with unsulfonated diazo compounds, such as diazotized aniline. For use in dyeing acetate silk the dyestuff is ground in the form of its moist press cake with a protective colloid, for instance sulfite cellulose liquor.

British Patent No. 256,281 to R. F. Thomas, J. Thomas, and Scottish Dyes, covers the nitration of bz.-halogenated benzanthrones with concentrated nitric acid in nitrobenzene solution. The nitro compound is reduced with zinc dust and concentrated hydrochloric or sulfuric acid in aniline or pyridine solution. The amino compound formed has a slight affinity for acetate silk and can be used as an intermediate product for other dyes. Halogenated alkyloxybenzanthrones are obtained by replacing the amino group by a hydroxyl group, and then alkylating with an alkyl sulfate in the presence of nitrobenzene. Fusion with alcoholic potash yields products, probably alkyloxyisodibenzanthrones, which dye cotton, from a violet-blue vat, a reddish-blue color of excellent fastness to light, washing, and bleaching.

British Patent No. 257,353, June 4, 1925, to the British Dyestuffs Corporation, W. H. Perkin and C. Hollins, states that substances which are probably anthraquinonyliminoanthrones are obtained by the condensation of an anthraquinone derivative contain-

ing a primary amino group with aminoanthraquinone, diaminoanthraquinones or their simple derivatives, such as diaminoanthrarufin and diaminochrysazin, in the presence of anhydrous calcium chloride or iodine as condensing agent at 200 to 300° C. The resulting products are not vat dyestuffs, but have a good affinity for acetate silk when applied direct from suspension in water, with or without the addition of dispersing agents.

Under the conditions mentioned 2 molecules of $\alpha$-aminoanthraquinone give a deep reddish-orange dyestuff. One molecule of $\alpha$-amino- and 1 molecule of 1, 4-diaminoanthraquinone a crimson direct, or a brownish-orange from a vat; $\alpha$-amino- and 1, 5-diaminoanthraquinone a brownish-orange. $\alpha$-Amino- and 1,8-diaminoanthraquinone a brick-red; $\alpha$-aminoanthraquinone and diaminoanthrarufin give a bright golden-brown. $B$-Aminoanthrarufin and diaminochrysazin give a drab. Equimolecular proportions of the compounds are finely ground with an equal weight of dry calcium chloride, and the mixture is heated at 200 or 250° C. for 1.5 to 3 hours. The small sublimate of aminoanthraquinone is removed and the bulk boiled with water to remove calcium chloride. The insoluble residue may be used directly, or after purification by dissolving in hot acetic acid and again precipitating with water.

British Patent No. 258,960, July 4, 1925, to the British Alizarine Company and C. M. Barnard covers the condensation of aminoanthraquinones and -benzanthrones with citric acid. For example, 20 grams of 1,4-diaminoanthraquinone are boiled with 80 grams of crystallized citric acid under a reflux for an hour, without a diluent. The condenser is then removed and the heating continued at 150° C. until a sample is completely soluble in sodium carbonate solution. The melt is then poured into 500 cubic centimeters of hot water, boiled, cooled, and filtered. The solid is dissolved in sodium carbonate solution or aqueous ammonia and the dye salted out or the solution evaporated to crystallization. The product dyes acetate silk a magenta color.

German Patent No. 303,121, August 8, 1916, to S. Aschkenasi is of interest in that it appears to antedate the use of some of these dispersing agents in connection with dyeing. Probably the method covered by this patent could be used in the preparation of

dispersol baths of vat or other insoluble dyes for use on acetate silk. This patent states that pastes of insoluble dyestuffs may be prepared by the addition of so-called "fat splitting" agents, such as Twitchell reagent, hydroricinoleic acid, naphthalene sulfonic acid splitter, etc. Indigo pastes may be prepared by adding one to three per cent of the fat splitter, on the weight of the dye, and stirring with water. The preparation of dye pastes with Turkon oil and other fatty derivatives is discussed, but it is claimed that at least fourteen times as much Turkon oil is required to give the same emulsifying action as the fat splitters, therefore the latter are more suitable for concentrated pastes.

The splitters may also be used as an addition to the dye bath to produce emulsification and thus allow the use of neutral or acid hydrosulfite vats. In this method, the splitter is added to the ordinary alkaline vat, after reduction by hydrosulfite at a temperature of not over 40° C. (104° F.). In the case of Indigo, the addition of 1 to 3 per cent of Twitchell reagent, on the weight of Indigo, is recommended. Thioindigo Scarlet is also mentioned as particularly suited for application by this method.

Clavel in United States Patent No. 1,517,709, December 2, 1924, covers the application of dyes in suspension to acetate silk and cotton or other acetate silk unions. In this process the cotton may be dyed to shade in the usual manner by a sulfonated dye which has no affinity for acetate silk. After rinsing, the acetate silk is dyed in a bath containing an insoluble dye such as Induline in suspension, in the presence of acetic acid at about 60 to 72° C. (140 to 160° F.). The dyed fabric is given a final treatment at 32° C. (90° F.) in a bath containing acetic or formic acid and an emulsion containing olive oil and olive-oil soap. The dyeing process may be reversed if desired, so as to dye the acetate silk first.

The preparation of the compounds mentioned in British Patent No. 214,765 is covered by United States Patent No. 1,528,470, March 3, 1925, to H. A. E. Drescher and J. Thomas. Halogen derivatives of anthraquinone are treated with an imide of a dibasic acid, such as phthalimide, in the presence of copper and an acid absorber, such as sodium acetate, at approximately 180 to 200° C. in order to eliminate the halogen in the form of an acid

and form another derivative from the anthraquinone and the imide. This product can be treated with an acid, such as sulfuric acid, to regenerate the dibasic acid and an amino derivative of anthraquinone formed. Numerous examples are given, including the preparation of 1-phthalimidoanthraquinone from 1-chloroanthraquinone and its conversion into 1-aminoanthraquinone; production of 1, 5-diphthalimidoanthraquinone and its conversion into, 1, 5-diaminoanthraquinone; 1-chloro-5-phthalimidoanthraquinone from 1, 5-dichloroanthraquinone and its conversion into 1-chloro-5-aminoanthraquinone; 1-phthalimido-2-nitroanthraquinone from 1-chloro-2-nitroanthraquinone and its conversion into 1-amino-2-nitroanthraquinone; 1-amino-2-methyl-4-phthalimidoanthraquinone from 1-amino-2-methyl-4-bromoanthraquinone and its conversion into diamino-2-methylanthraquinone; 1-methylamino-4-phthalimidoanthraquinone from 1-methylamino-4-bromoanthraquinone and its conversion into 1-methylamino-4-aminoanthraquinone; 1-phthalimido-2-aminoanthraquinone from 1-chloro-2-aminoanthraquinone and its conversion into 1,2-diamoanthraquinone; 2-phthalimidoanthraquinone from 2-bromoanthraquinone and its conversion into 2-aminoanthraquinone; and 1-succinimidoanthraquinone from 1-chloroanthraquinone.

United States Patent No. 1,532,921, April 7, 1925, to F. Munz, utilizes ordinary soaps, sulfonated products, Turkey-red oils, monosolvol, etc., as well as organic solvents, such as benzene and its homologues, hydrated carbohydrates, chlorocarbohydrates and similar substances, as solvents for the insoluble products to be applied by the dispersol method. He states that alkalies, such as soda ash and ammonia, frequently assist in solubilizing the dyes. For example, acetate silk may be dyed a yellow shade with 2 per cent, on the weight of the fabric, of dimethylamidoazobenzene, 4 per cent of Turkey-red oil, 4 per cent of solvent naphtha and 0.4 per cent of soda. These are boiled with 40 to 50 times their weight of water and added to the dye bath at 80 to 85° C. (176 to 185° F.). The acetate silk is dyed for about three-quarters of an hour to exhaust the bath, rinsed and finished in a dilute acetic acid bath.

In the same manner, a deep black may be obtained on acetate silk with 3 per cent of the dyestuff derived from *o*-anisidine-*a*-

naphthylamine, 8 per cent of common curd soap, 5 per cent of tetralin and 1.5 per cent of soda ash. This is handled in the same manner as the above but at 60 to 65° C. (140 to 149° F.), then diazotized and developed with *B*-hydroxynaphthoic acid.

A clear blue color on acetate silk may be obtained in the same manner but using 0.5 per cent of dianisidine, 2 per cent of soap, 1.5 per cent of tetralin and 0.5 per cent of soda ash. This is diazotized and developed with *B*-hydroxynaphthoic acid also, as above.

United States Patent No. 1,610,961 to R. Metzger, assigned to the Interessen Gemeinschaft, covers the application of insoluble or difficultly soluble dyestuffs, bases, amino compounds, naphthols. etc., to acetate silk by the dispersol process, using the catalytic organic fat saponifiers as the dispersing medium. Suitable compounds are, Twitchell's reagent, naphthenic acids, mixed fatty acid and naphthalenesulfonic acids, and also the alkylated naphthalenesulfonic acids such as isopropylated napththalene, or butylated or isobutylated naphthalenesulfonic acids, or the salts thereof.

For application, the dyestuff or other compound to be applied to the acetate silk is dissolved or dispersed in the above suitable reagent to form the usual concentrated solution which is added to the dye bath; or the dye bath may be prepared directly with the dyestuff while adding the dispersing agent.

For example, 100 parts of acetate silk may be dyed a strongly fluorescent yellow by 2 parts of 3-aminobenzanthrone dissolved or dispersed in a suitable amount of Twitchell's reagent. This is added to 2000 to 3000 parts of water containing a little soap and the goods entered at 60 to 70° C. In the same manner a red color may be obtained with 1 per cent of benzoyl-1-aminobenzanthrone.

One per cent of 5-nitro-1,4-diaminoanthraquinone, on the weight of acetate silk, gives a violet color when dissolved in concentrated aqueous solution of sodium diisopropylnaphthalenesulfonate and added to a dye bath containing 20 grams per liter of concentrated neutral sulfite waste liquor.

1-Amino-4-anilidoanthraquinone dissolved in butylated naphthalenesulfonic acid, obtained by condensing normal butanol with

naphthalenesulfonic acid, gives a bright blue color. About 10 grams of the sulfonic acid, per liter of dye bath, should be used. *a*-Naphthylamine (diazotized) with *m*-phenylenediamine, *a*-amino-*a*-naphthoquinone, 8-nitro-2-aminonaphthalene, Methyl Violet base, *a*-naphthylamine (diazotized) with *p*-hydroxybenzoic acid, are also mentioned. Also see German Patent No. 303,121, and British Patents No. 224,925, and No. 242,393.

### *Dispersol Dyes on Other Fibers*

While the dispersol type of dyes were developed especially for use on acetate silk, at least some of them are applicable to other fibers. In the discussion of the Celantene patents, it was mentioned that certain of the products are applicable to cellulose fibers other than cotton. The following patents cover the application of dyes of this class to straw, jute, hemp, esparto, raffia, flax, ramie, wool, true silk, "resisted" or "immunized" cotton, etc.

According to British Patent No. 228,634, November 8, 1923, to J. S. Wilson, J. Thomas, and Scottish Dyes, wool is dyed by immersion in aqueous suspensions of mono-, di- or triaminoanthraquinones, alkylaminoanthraquinones, or substituted derivatives of these substances, but excluding hydroxyl derivatives or related acid dyestuffs. Dispersing agents such as alcohol and cresol are used. For example, one hundred pounds of thoroughly wet-out woolen yarn may be dyed in a 200 to 400 gallon (British) dye bath containing 2 to 4 pounds of alcohol and 1 pound of 1-amino-2-methylanthraquinone at 90° C. (194° F.) for a half to three-quarters of an hour. The dyed yarn should be rinsed to remove undissolved dyestuff and dried. Suitable dyestuffs are 1-methylaminoanthraquinone, 2-aminoanthraquinone, 1-chloro-2-aminoanthraquinone, 1, 4-diaminoanthraquinone, 1-methylamino-4-aminoanthraquinone and 1-methylamino-4-amino-2-bromoanthraquinone.

British Patent No. 230,130, October 29, 1923, to J. S. Wilson, J. Thomas, and Scottish Dyes states that true silk may be dyed by immersion in an aqueous suspension of monoamino-, diamino-, triamino-, or alkylaminoanthraquinones and their derivatives, but excluding sulfonated or carboxylated derivaties, which are usually

regarded as true silk dyestuffs. Suitable products are 1-methylamino-, 1-amino-2-methyl-, 2-amino-, 1,4-diamino-, 1-methylamino-4-amino-, and triamino-anthraquinone. For example, 5 parts of true silk may be dyed a bluish-red color by immersion at 80 to 90° C. (176 to 194° F.) for 45 minutes in 100 parts of water containing 0.5 part of a 10 per cent paste of 1-methylamino-anthraquinone. After dyeing the fabric should be rinsed and lightly soaped in the usual manner. These dyes are also applicable to unions containing true silk.

British Patent No. 238,590, April 24, 1924, to R. F. Thompson, J. Thomas, and Scottish Dyes, covers the application of similar anthraquinone derivatives to cellulose and ligno-cellulose fibers, such as straw, jute, hemp, esparto, raffia, flax and ramie, but not cotton. These fibers are dyed fast shades by immersion in hot alkaline or acid liquors containing suitable aminoanthraquinones or their derivatives in suspension or in solution. For instance, straw is dyed an orange shade of good fastness to light by treating it for an hour in a boiling alkaline dye bath consisting of 100 gallons of water, 2 pounds of soda ash, and 5 pounds of a 10 per cent paste of 1-amino-2-methylanthraquinone. Thirty to forty pounds of jute, hemp, straw or tagel may be dyed a reddish-violet shade of excellent fastness to light by boiling for an hour in a dye bath containing 100 gallons of water, 30 pounds of acetic acid and 10 pounds of a 10 per cent paste of 1,4-diaminoanthraquinone. Suitable dyestuffs include 1-chloro-2-aminoanthraquinone (yellow), 1-methylaminoanthraquinone, and the nitration product of hexa-aminodianthraquinonylthio-ether (blue).

According to British Patent No. 246,609, November 17, 1924, to A. E. Woodhead and the Sandoz Chemical Company, immunized or resisted cotton (see British Patents No. 195,619, No. 233,704, No. 241,854 and German Patent No. 346,883), prepared by treating ordinary cotton with alcoholic sodium hydroxide and *p*-toluenesulfochloride, may be dyed by means of insoluble or difficulty soluble dyestuffs which have been solubilized by pretreatment with suitable dispersing agents, such as the higher fatty acids or their sulfo-derivatives, their alkali-metal or ammonium salts. The methods of dyeing are similar to those generally used for acetate

silk except that the temperature of the bath is preferably 75 to 95° C. (167 to 203° F.).

This patent covers the use of the following dyestuffs in this manner: azo dyestuffs prepared from nitroanilines, dinitroanilines, nitrotoluenes, nitroxylidenes, anisidines, chloroanisidines, nitroanisidines, phenetidines, chlorophenetidines, nitrophenetidines, or chloronitroanilines diazotized and coupled with aniline, methylaniline, dimethylaniline, ethyl- or diethylaniline, methylethylaniline, diphenylamine, methyl- or ethyl-diphenylamine, *m*-toluidine or *p*-xylidine. Aniline, chloroanilines, dinitroanilines, toluidines, xylidines, nitrotoluidines, nitroxylidines, anisidines, chloro- or nitro-phenetidines diazotized and coupled with *a*- or *B*-naphthylamine or their methyl, dimethyl, ethyl, diethyl, methylphenyl, or ethylphenyl derivatives. *a*- or *B*-naphthylamines, or their chloro- or nitro-derivatives diazotized and coupled with aniline or their alkyl- or aryl-aniline or naphthylamine derivatives mentioned above, or *a*- or *B*-naphthylamine. Naphthols, resorcinol, *B*-hydroxynaphthoic acid and its anilide, toluidide, and similar derivatives coupled with diazotized amino bases such as *m*-nitroaniline and *a*-naphthylamine. This method of dyeing allows the production of two-color effects in union fabrics containing ordinary cotton and other fibers, together with immunized cotton.

Apparently, if not too expensive, this new process of resisting or immunizing cotton to the direct cotton dyes offers a new method of obtaining two color effects, very probably in one dye bath. If the extent of the change (immunizing) process may be varied within wide limits, probably it will be possible to obtain a variety of products each one of which may dye in more or less different depths of shade in the one dye bath. In fact this very multiplicity of possible products may be a detriment to the whole process, unless it is possible to so control the process as always to get the same dyeing properties in the "immunized" product. Undoubtedly this treated fiber will be dyed, more or less, by many acetate silk dyes of the dispersol class, but the shade of the immunized cotton and acetate silk, from the same dye bath, will probably be quite different. It undoubtedly offers another method of obtaining a variety of color effects in textiles.

# CHAPTER XXIV

## COLOR PRINTS AND DISCHARGES ON ACETATE SILK AND ACETATE SILK UNIONS

THE printing properties of the various groups of dyes which are applicable to acetate silk have been briefly mentioned in connection with the discussion of each class of dyestuffs. Davies,[1] who is quite an authority on this subject, says that to a certain degree the printing of acetate silk offers but little difficulty, but that this can be regarded as true only if we are considering the direct printing of an all-acetate-silk piece of goods. The statement has frequently appeared in the literature that the printing of acetate silk is even simpler than the dyeing and quite a variety of processes are used.

In applying the basic, certain acid, mordant, vat, and many other special dyes which have an affinity for acetate silk, formulas similar to those used for the application of these dyes to other fibers will frequently serve without much change. Glucose, British gum, and tragacanth have been recommended as thickening agents for acetate silk printing pastes. Even the direct cotton dyes, which have no affinity for acetate silk, can be printed on this fiber with an alkaline thickener and steamed to produce prints of ordinary direct color fastness. In this case the direct color is fixed solely by the local or surface saponification of the printed portions of the acetate silk, due to the alkalinity of the paste.[a]

[a] The direct color printing paste may be prepared as follows:[5]
2 grams of direct dyestuff dissolved in
40 cubic centimeters of water and
1 gram of sodium phosphate.
This mixture is added to 80 cubic centimeters of 60 per cent gum arabic thickening, and finally 20 cubic centimeters of 76° Tw. sodium hydroxide solution are added. The goods are printed, aged at 101° C. (214° F.) for 30 minutes with dry steam, and washed off.

In steaming acetate silk materials, care must be taken to insure the use of only dry steam, otherwise the moisture present may blind the fiber.

Schneevoigt[6] prints acetate silk with alkaline pastes of the vat dyes and states that the local saponification of the fiber occurs without a serious loss of luster. He also mentions a superficial saponification before the printing. The basic dyes are equally fast on this superficially saponified acetate silk and cotton.

In fact many color pastes for acetate silk printing contain sodium hydroxide, the prints being fixed by steaming. This of course causes a local saponification of the acetate silk fiber, which in most cases is not objectionable in the case of small printed designs, as there is very little alteration in appearance or loss of weight, and it allows the use of a much wider range of dyestuffs. These alkaline pastes may also be used for printing acetate silk-cotton unions, covering both fibers in the one operation.

Cotton[2] mentions that in Europe they are dyeing cotton-acetate silk combinations with direct cotton dyes, which of course leaves the acetate white, and then printing on a basic color discharge. This gives a very beautiful shot effect. The same kind of effects are also obtainable on acetate silk-viscose unions, or combinations with the other rayons.

In printing the basic dyes on acetate silk, as well as other dyes which have an affinity for this fiber, and where alkaline pastes are not used, acetic acid (10%) is frequently added to the printing paste.[5] This acts as a solvent or swelling agent on the fiber, which serves to fix the color. The prints may be steamed without pressure, and washed. The basic dye prints may be fixed with tannin in the ordinary way.[4] Also see British Patents No. 242,711, and No. 244,143, of Chapter XXIII, which refer to the use of special compounds in printing acetate silk.

According to J. Pokorny[3] resorcinol may be useful in certain printing operations on acetate silk. He states that resorcinol is a solvent for basic dyestuffs and their lakes formed with tannic acid and various inorganic salts. Pastes prepared in this manner, when printed on fabrics containing acetate silk, usually partially deacetylate the acetate silk and generally give deep shades. It is possible that some of the Gallopont dyes recently developed by the Du Pont Company may be applicable in this manner, as they are probably compounds of basic dyes with suitable mordants, in a special solvent (not resorcinol).

In connection with the use of solvents in printing acetate silk and unions containing this fiber, the British Patent No. 223,888 to J. R. Geigy Company may be of interest. This patent covers the use of ethyleneglycol and ethylenechlorhydrin as solvents for

use in printing pastes, in place of gylcerol, acetin, phenol, aniline, alcohol, ethylenethiodiglycol, etc. At least some of the compounds mentioned are suitable for use alone or in combinations with other compounds either as solvents or swelling agents for acetate silk. By suitably combining these in a properly prepared printing paste, undoubtedly some very interesting effects could be obtained on acetate silk unions. Geigy claims that ethyleneglycol and ethylenechlorhydrin have a high solvent action towards many dyestuffs and aid the penetration of the printing pastes very materially.

The printing of chrome dyes on acetate silk-cotton unions is not generally very satisfactory, as the long steaming necessary to fix the dyestuff usually destroys the luster of the acetate silk. Those which are fixed by only a short steaming may be applied in the regular way.

Ellis[4] states that the three best types of dyes for the direct printing of Celanese are the basic, S.R.A., and Indigoid dyestuffs. All of these are fixed very well without hydrolysis of the fiber, the S.R.A. and Indigoid dyes directly, by a simple steaming or ageing. Another method of printing the vat and sulfur dyes on acetate silk is by means of Sulfoxite C or Rongalite C, according to the following formula.[1]

*Method No. 82: Color Printing Paste for Sulfur or Vat Dyes on Acetate Silk.*

10 grams vat dye paste,
2.5 to 5 grams sulfoxite C.
3 cubic centimeters glycerol.
25 cubic centimeters 76° Tw. sodium hydroxide solution, and
75 cubic centimeters of British gum paste, 6 lbs. per gal.

Print and age for 5 minutes at 101° C. (214° F.). Where the oxidation has not been complete, an after-treatment with dilute hypochlorite solution, as in Method No. 15 or No. 16. but more dilute, may be given. Rinse well and soap at about 82° C. (180° F.).[b]

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[b]Another formula[5] for vat dye printing paste is:
10 to 15% of vat dye paste,
3% glycerol,

British Patent No. 256,238 to the Soc. Anon. des Etablissements Petitdidier, St. Denis, France, covers the printing of fabrics containing acetate silk and cotton or viscose. (1) The fabric is printed in the usual manner with a dyestuff such as one having an anthraquinone base, certain acid dyestuffs such as Citronine, or a basic dyestuff mordanted with Acetanol. (2) The printed fabric is steamed to fix the dyestuff on the acetate silk. (3) The fabric is rinsed, whereby a portion of the coloring matter is removed from the cotton or viscose. (4) The fabric is optionally steeped in a dilute solution of hydrosulfite in order to remove all color from the cotton or viscose silk. The fabric may be finally dyed with a dyestuff which has an affinity for the cotton without appreciably staining the acetate silk.

Ellis[4] states that the "Rapid Fast"[c] colors may also be printed on acetate silk, and suggests Diphenyl Black Base for black prints, with rather more oxidizing agent than is used for the same purpose on cotton. The usual chlorate-prussiate method usually gives good results. Also see Methods No. 59 and No. 60.

### *Ionamine Prints*

The Ionamines have been successfully printed on acetate silk by means of a thickened dye paste containing an organic acid. After printing, the material is dried, steamed for 5 minutes or longer without pressure, and washed. It may then be diazotized and developed if necessary. While the shades are usually very good, they do not always have the desired fastness to washing. Typical examples of suitable dyestuffs are:[5] Ionamine A, Ionamine B, Ionamine MA, Ionamine GA, and Ionamine Red KA. Also see Chapter XX.

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*(Footnote continued)*

4% of 76° Tw. sodium hydroxide solution,
5% sodium carbonate,
5% potassium carbonate,
2.5% solution salt,
7 to 8% Formosul, and
60 to 65% British gum thickening (3 lbs. per gal.).

Print, age, wash, and soap as in method No. 82. Sulfur dyes may be applied by a similar process and Thional Printing Black No. 2, Thional Brown GD, and Thionol Green B are mentioned as suitable.

[c] See Chapter XVI.

### *Developed Colors*

As a class the developed colors, such as are obtained with the Azonines, Azoniles, Silkons, Azoles, etc., are not satisfactory for printing purposes on acetate silk, as the white grounds usually become more or less stained during the development.[6]

### *Dispersol Prints*

The dispersol dyes (S. R. A.'s, Duranols, Celatenes, Celanthrenes, and Dispersols) may be effectively printed on acetate silk materials by simply thickening the dye paste, with or without a little ammonium thiocyanate, printing and steaming without pressure for 10 to 30 minutes, with only minor variations from the usual printing practice. The addition of about a half pound of soluble oil to each hundred pounds of printing paste generally improves the shade. The S. R. A. dyes on Celanese are often extremely fast to soaping. Possibly the reducing substances, such as stannous chloride or hydrosulfite are best suited for resisting the dispersol dyes, but this type of dye is not particularly adapted for resist work.[d]

### *Printing Unions*

In printing acetate silk-cotton unions, pleasing two-color effects may frequently be obtained by applying suitable CR direct cotton dyes and dispersol dyes mixed in the one printing paste as in Method No. 83. In this manner each of the dyes colors its particular fiber only, and the unfixed dye is later rinsed from the fabric.

*Method No. 83: Two-Color Acetate Silk-Cotton Union Printing Paste.*

2 grams CR dyestuff dissolved in
10 grams glycerol,
23 grams hot water, and
60 grams British gum thickener.

[d] Satisfactory prints on acetate silk have been obtained with a printing paste containing 50 grams of a suitable anthraquinone dye, such as Yellow 3G Extra (Badische), Yellow R, Rose R, or Violet B, 50 grams of Turkey-red oil, 50 grams of glycerol, 50 grams of Ludigol (*m*-nitrobenzenesulfonic acid), and 800 grams of a British gum and starch thickener. The prints are steamed for 5 minutes in a Mather-Platt, without pressure, as blinding may occur on pressure steaming.[6]

When dissolved and cool add 5 grams of dispersol (Duranol) dye paste. Print, steam 15 minutes at 100° C. (212° F.) without pressure and wash off.

*Discharge Prints*

Davies[1] states that dischargeable direct cotton colors are being dyed on acetate silk which has been saponified either with or without a protective medium in the saponification bath. Such colors are dischargeable with the usual reducing agents, such as a 10 per cent solution of Formopon (sodium formaldehyde sulfoxylate), though generally somewhat stronger discharge pastes must be used and care must be taken in the washing to prevent the whites from being sullied.

When dealing with unsaponified acetate silk, it has been almost impossible to obtain good white discharges, and therefore colored discharges have been the only really satisfactory ones produced. The following dyes are suitable for ground colors if the goods are to be subsequently discharged with hydrosulfite:

Cellutyl Fast Golden Yellow
Cellutyl Orange 2R
Cellutyl Fast Orange G
Cellutyl Sky Blue
Cellutyl Fast Red D
Cellutyl Fast Lilac
Acronol Brilliant Blue

The regular basic dyes which are commonly used with the sulfoxylates for color discharges can be used for the production of colored discharges on acetate silk. Schneevoigt[6] recommends the addition of resorcinol to acetate silk discharge printing pastes containing Rongalite for use in obtaining white discharges on basic colors.

The following colors on acetate silk may be discharged to a satisfactory white by means of a chlorate discharge:

Duranol Blue G in light shades
Duranol Red 2B
Cellutyl Fast Orange R
Cellutyl Bright Yellow
Cellutyl Bright Red
Cellutyl Bright Green B and Y
Cellutyl Sky Blue
Cellutyl Fast Blue
Cellutyl Fast Gray
Cellutyl Fast Lilac
Methyl Violet 2B and 10B
Acridine Orange L

It is a peculiar fact that certain colors of this class which theoretically should be readily dischargeable with sulfoxylates and are, where applicable, easily discharged on other fibers, cannot be discharged by the ordinary sulfoxylate method when dyed on acetate silk.

The discharge printing of the dispersol dyes on acetate has not been very satisfactory, as the reduction of these colors by the usual hydrosulfite or sulfoxylate process, such as commonly used on cotton, silk, and wool, is not generally effective with the dispersol type of dyes on acetate silk; however, some members of the group respond to this treatment better than others. The British Dyestuffs Corporation have found that the addition of thiocyanates to the reduction discharge printing paste containing sodium sulfoxylate, aids materially in the reduction of many colors which it was formerly impossible to discharge for some unknown reason. Davies[1] recommends the calcium thiocynate for this process, as in the following formula.

*Method No. 84: Discharge Printing Paste for Acetate Silk.* Fifteen to 20 parts sodium sulfoxylate (Formosol, Rongalite, etc.) are dissolved in 75 to 70 parts of a solution of 30 parts of gum tragacanth in 1000 parts of water, and cooled. Ten parts of 88° Tw. calcium thiocyanate solution are then added.[e]

The dyed fabric, without previous preparation, is printed, dried, and aged for 3 to 5 minutes in the Mather-Platt ager at 101° C. (214° F.). It is then well washed in water at 60° C. (140° F.) and dried.

By this method, the following colors give white discharges on acetate silk:

Cellutyl Fast Yellow C
Cellutyl Fast Golden Orange
Cellutyl Orange 2R
Cellutyl Fast Orange Yellow
Cellutyl Fast Orange G and GK
Cellutyl Fast Red D
Cellutyl Sky Blue
Acronol Brilliant Blue
Ionamine A (only when dyed direct)
Ionamine B (only when dyed direct)
Ionamine MA (only when dyed direct)
Ionamine GA (only when dyed direct)
Ionamine B developed with *B*-hydroxynaphthoic acid
Ionamine GA developed with *B*-hydroxynaphthoic acid
Ionamine Red KA
Dispersol Yellow 3G

[e] This process is covered by British Patent No. 262,254, November 25, 1925, to L. Smith and the British Dyestuff Corporation, which states that clear white and colored discharge effects on acetate silk dyed with those dyes commonly used for this material are obtained in the usual manner by means of reducing agents containing sodium formaldehydesulfoxylate, provided that thiocyanates such as calcium, barium, and ammonium thiocyanate are present. A satisfactory discharge paste contains 15 grams of sodium formaldehydesulfoxylate, 70 grams of 3 per cent gum tragacanth solution, and 10 grams of an aqueous solution of calcium thiocyanate (specific gravity 1.44).

Where the above dyes are combined with dischargeable direct cotton dyes on acetate silk-cotton unions, Method No. 84 gives white effects on both fibers.

The following substantive dyestuffs, which leave acetate silk either white or only slightly stained, are suitable for white discharges on the accompanying cotton:

Pyramine Yellow G
Pyramine Brilliant Orange 3RS
Oxamine Light Red 4B
Oxamine Light Red E8B (for light and medium shades)
Oxamine Brilliant Red B (for light and medium shades)
Cotton Fast Red 8BS
Oxamine Light Pink BX and BBX
Cotton Pink BN and GN
Oxamine Brilliant Light Violet B and RR
Oxamine Blue B, 3B and GN
Oxamine Light Blue G (for light and medium shades)
Oxamine Light Blue B and BG
Oxamine Pure Blue 5B and 6B
Oxamine Black BHN and RN
Oxamine Light Gray EB
Oxamine Dark Blue BG
Oxamine Blue 4B (for light and medium shades)
Cotton Black AC

The following give white discharges in pale shades but in medium and full shades are suitable only for colored discharges:

Oxamine Fast Yellow B
Stilbene Yellow GX and 3GX
Cotton Orange G and R
Thiazine Brown G and R
Thiazine Red GXX and R
Oxamine Violet
Burl Black B

The following acid dyestuffs which leave acetate silk either white or only slightly stained are suitable for white discharges on the accompanying animal fibers:

Wool Fast Yellow G
Supramine Yellow R
Orange II
Anthosine 3B
Scarlet RR
Supramine Red B
Neptune Green S10G
Light Green SF Yellowish

The following are adapted for the production of colored discharges:

Quinoline Yellow and Extra
Acid Rhodamine BG
Azocarmine BX
Acid Violet 4RN

### *Special Printed Effects*

British Patent No. 215,860, February 22, 1923, to the Calico Printers' Association and F. Roberts, covers the production of pattern effects on fabrics containing rayon, including acetate silk, by means of mercerizing agents other than sodium hydroxide, such as sulfuric, hydrochloric, phosphoric, or nitric acid, or zinc chlo-

ride, cuprammonium, or calcium thiocyanate solution. The "mercerizing" agent may be directly printed on the fabric, or the fabric may be first printed with a resist, such as starch or British gum, and then immersed in the mercerizing agent. When the fabric contains acetate silk, and the latter method is employed, the limits of treatment are: 1 to 5 seconds with 80 to 168° Tw. (1.140 to 1.84 sp. gr.) sulfuric acid at 13° C. (55° F.); 2 seconds to 2 hours with phosphoric acid of 129 to 160° Tw. (1.65 to 1.80 sp. gr.) at 12 to 93° C. (53 to 200° F.); 1 to 15 seconds in 26 to 40° Tw. (1.13 to 1.20 sp. gr.) hydrochloric acid at 13° C. (55° F.); 1 to 5 seconds in 60 to 84° Tw. (1.30 to 1.42 sp. gr.) nitric acid at 13° C.; 0 to 15 minutes in cuprammonium solutions containing 2.5 to 5.0 per cent of copper at 13 to 82° C. (55 to 180° F.); and 2 seconds to 1 hour in calcium thiocyanate solutions containing 25 to 90 grams per 100 cubic centimeters of solution at 13° C.

According to British Patent No. 237,909, July 29, 1924, to Heberlein and Company, printed effects on unions of acetate silk with mercerized or unmercerized cotton, wool, silk, or the older rayons, may be obtained by printing the material with a resist such as glue, alcoholic shellac solution, or/and a thickened solution of sodium or potassium carbonate or hydroxide, steaming if necessary, and then treating the goods with a solvent for the unresisted acetate silk, such as chloroform, acetone, pyridine or epichlorohydrin.

Suitable reserves for this process are materials which have a mechanical protective effect or have the property of chemically changing the parts of the acetate silk with which they come in contact. Mechanical protective agents may comprise materials such as glue or shellac, which are insoluble in the acetate silk solvents used. Chemical protective agents comprise saponifying materials such as sodium or potassium hydroxides or carbonates. The reserve effect may be further enhanced by dyeing or color printing, as by the application of suitable vat dyes in the alkaline printing paste, and after the removal of the unreserved acetate silk, the ground may be dyed a contrasting color. Alkaline reserves containing a suitable direct cotton color discharge may be printed on dyed materials, etc.

Another printed effect is covered by United States Patent No. 1,588,951, June 15, 1926, to C. Dreyfus, assignor to the American Cellulose and Chemical Manufacturing Co. This states that union fabrics containing acetate silk or similar cellulose derivatives may be printed with a mixture containing a solvent for the ester, such as lactic acid, an inert powder, such as infusorial earth, and a thickening agent such as dextrin. The printed fabric is maintained at a temperature not exceeding 125° C. until at least a portion of the acetate silk in the printed parts may be removed by washing with water. Also see Chapter XXXVIII for other printed effects.

*References*

[1] H. R. Davies, *American Dyestuff Reporter 14*, 887-9 (1925) ; and *15*, 202 (1926).
[2] W. Cotton, *American Dyestuff Reporter 15*, 331 (1926).
[3] J. Pokorny, *Rev. gen. mat. col. 29*, 224 (1925).
[4] G. H. Ellis, *J. Soc. Dyers and Colourists 42*, 184-6 (1926).
[5] British Dyestuff Corporation, "The Dyeing and Printing of Artificial Silks," (1926).
[6] A. Schneevoigt, *Textilber. 7*, 354 (1926).
[7] W. Milne, *American Dyestuff Reporter 15*, 886 (1926).

## CHAPTER XXV

# DYEING UNION MATERIALS OF ACETATE SILK WITH OTHER FIBERS, OR MATERIALS CONTAINING ACETATE SILK WHITE OR COLORED EFFECTS

It is of course very evident that before attempting to dye combinations of acetate silk with any other fiber or fibers, the dyer should be proficient in dyeing all fibers concerned alone, as well as thoroughly familiar with all of the dyestuffs to be employed, their characteristics, cross-dyeing and staining properties on the various fibers, etc. Without this complete understanding of the subject, it is useless to hope for satisfactory results on a commercial scale. For this reason it is only logical that the discussion on dyeing acetate silk unions should follow that on dyeing acetate silk alone.

In the dyeing of union materials, every difficulty encountered in dyeing the component fibers of the mixture is again met, but often in an aggravated form, due to the restrictions caused by the other fiber or fibers present. Thus, in dyeing the cotton of cotton-acetate silk combinations with direct cotton dyes, even where the acetate silk is present only as effect threads, the alkalinity of the dye bath must be restricted in order to avoid the saponification of the acetate silk.[a] Again in dyeing the wool in wool-acetate silk mixtures with acid dyes, both the temperature and acidity of the dye bath are subject to restrictions, due to the presence of the acetate silk.[b]

At the present time, one of the largest uses for acetate silk appears to be in obtaining multi-color effects, often in widely contrasting colors, in one dyeing process, and on account of the restrictions placed upon the dyeing processes by the properties of the fibers involved, a very careful study of the dyestuffs available, including all of their properties such as cross-dyeing, ex-

[a] See Chapter XIX.

[b] As Lustron is more sensitive to acids than Celanese, particular care is necessary in the control of acid baths to be used on materials containing Lustron.

haustion, hydrogen ion concentration of the dye bath, staining accompanying fibers, fastness, etc., must be made. It is also obvious, from a study of the properties of the different brands of acetate silk, that the properties of the particular variety of acetate silk present must not be neglected. For example, Lustron has a greater affinity for the basic dyes than Celanese or Rhodiaseta, and withstands the action of a boiling dye bath for some time. This latter may be a considerable factor in the application of certain neutral dyeing acid dyes to wool in wool-acetate silk combinations.

However in spite of all these difficulties, a wide variety of two or even more, contrasting color effects are obtainable on acetate silk unions containing all proportions of acetate silk, which meet all the usual fastness requirements, by the one dye bath process. Obviously, this is only possible by a careful study of all of the factors involved and dyestuffs available. Even more satisfactory results, to meet very exacting demands, are possible by the two bath process. In this latter process even incompatible dyes may be used and a much better result obtained due to a better control of the factors influencing the application of each dyestuff.

With all the drawbacks, three color combination effects upon three fiber materials are possible in some cases in a single bath, but are usually a matter of considerable manipulation and are not by any means uniformly satisfactory, as it is practically impossible to dye all three shades to sample. By means of the two or three bath method, even solid colors are obtainable on many three fiber combinations containing acetate silk. The difficulty in dyeing wool and true silk at the low temperatures recommended for Celanese and Rhodiaseta is of course recognized as one of the very considerable restrictions along this line. The use of Lustron, with its greater resistance to high temperatures in the dye bath, will obviate this restriction to some extent.

### *Protecting Acetate Silk in Boiling Solutions*

In this connection the recently announced methods of conserving the luster of Celanese and Rhodiaseta in boiling aqueous baths are of particular interest. It was formerly considered impossible

to treat materials containing these fibers at temperatures above about 85° C. (185° F.) in the presence of water without loss of luster and other valuable properties. British Patent No. 206,113[c] shows how true silk may be degummed in the presence of Rhodiaseta in a boiling soap bath and British Patent No. 246,879 covers the dyeing and other treatment of materials containing Celanese in boiling aqueous solutions. Both of these patents are based upon the use of a certain minimum quantity of suitable inorganic salts in the aqueous liquor. These salts appear to act as protective agents, very possibly by retarding the hydrolysis of the cellulose acetate, so that the bath may be boiled for some time without injury to the fiber. In this way it is possible to cross-dye Celanese unions with direct cotton or other dyes at the boil. Obviously in the case of unions containing Lustron, which withstands treatment in boiling water, this method is unnecessary.

*Method No. 85: Cross-Dyeing Celanese at the Boil.* Enter the union into the direct cotton dye bath at a temperature not over 82° C. (180° F.) and dye until the bath is nearly exhausted, with the usual addition of Glauber's salt. When the dye is nearly exhausted, add sufficient concentrated solution of Glauber's salt to bring the total amount of this constituent to about 30 per cent, on the weight of the dye bath. Raise the temperature to boiling and boil for an hour. In case only a half hour's boiling is necessary a slightly lower percentage of Glauber's salt may be used. For an hour's boiling, the dye bath should contain about 2.5 pounds of Glauber's salt per gallon of liquor. After this dyeing, rinse well and fill in the Celanese to shade in a second dye bath at a temperature below 80° C. (175° F.). The luster of the Celanese should be unaffected. It has also been recommended[1] to use a 10 per cent solution of ammonium sulfate in the same way, in place of the sodium salt.

This process is covered by British Patent No. 246,879, of June 31, 1924, to A. J. Hall and the Silver Springs Bleaching and Dyeing Company, which states that acetate silk may be treated for prolonged periods in boiling aqueous liquors without becoming curly and wool-like, and without loss of luster and transparency,

[c] See Chapter X.

if the liquor contains not less than a certain minimum amount of a protective salt, the minimum quantity being dependent on the particular salt or salts usd. Suitable salts include sodium, ammonium, calcium, magnesium, barium, aluminum, strontium, and potassium chlorides; ammonium, sodium, copper, magnesium, zinc, and potassium sulfates; sodium sulfite, alum, chrome alum, sodium chlorate, potassium oxalate, and sodium nitrate. The dyeing properties of the acetate silk are not altered by such treatment. In general, 10 to 30 per cent solutions of the protective salts are used and they are particularly useful in the treatment of acetate silk materials containing other fibers, or other treatments in which it is necessary to use boiling liquors, or other liquors at a temperature exceeding 85° C. (185° F.). The process has particular application in the dyeing of acetate silk-wool union textile materials. Canadian Patent No. 260,319, April 27, 1926, to H. Dreyfus appears to cover the same process. Also see British Patent No. 206,113.

Much has already been said concerning the dyeing of acetate silk unions under the subject of the various classes of dyes. In dyeing cotton or wool goods with an acetate silk thread stripe or effect, it is not always necessary and is sometimes not desirable to leave the acetate silk white. When this is the case an even wider range of direct, acid or other dyes than those mentioned may be used on the fibers accompanying the acetate silk. However, in case the acetate silk is stained by the dyes used on the other fibers, care must be taken in buying the dye that various shipments of the dye, even from the same manufacturer, stains the acetate silk to the same extent. For this reason, it is usually much safer and more satisfactory to use a cotton or wool dye which does not stain the acetate, and then dye the acetate silk stripe or effect with some other suitable dyestuff, in the same dye bath, if desired.

In selecting direct cotton or, in fact, dyes of any other class which do not stain acetate silk, it should be remembered that in the case of most of these dyes, it is not the direct dye itself which stains the acetate silk, but some uncombined base, basic impurity, or even a basic dye, the latter probably added for shading purposes. From this it can readily be seen that while one batch of a direct dye

may stain the acetate silk very little or not at all, the next lot, even from the same source, may vary considerably in this respect. Most of the special "acetate white" direct dyes offered on the market are merely a purified grade of some older and usually well known direct dye. The same statement applies to the acetate-white dyes of other classifications. For this reason, in buying direct dyes to be used on materials containing acetate silk, each shipment of dyestuff should be carefully tested out in the laboratory before its use is attempted in the plant.

Many direct cotton blacks stain acetate silk a yellow or orange color, due to the presence of basic yellow or orange dyes used to give depth and fullness. In this way, at least one hoisery-dyeing plant in America is using a direct dye which stains acetate silk on cotton-acetate silk so as to give two-colored-effect hoisery. In this case the color on the cotton and acetate silk are sufficiently different to give a good two-color effect in the one dye bath at an extremely low price. Possibly a dyestuff such as Chlorazol Black E Extra could be used for this purpose. However, while this scheme is very cheap, it will hardly be found satisfactory on the better class of goods which must be dyed to sample.

In connection with Chapter XIII on the Acid and Mordant Dyes on Acetate Silk, many acid dyes are mentioned which dye acetate silk, but which in most cases give a different shade, usually of the same color, on wool or true silk. A suitable selection of dyes from this group could be used for more or less contrasting shades on acetate silk-wool or true silk unions. By using a union dye which stains or dyes acetate silk on combinations of acetate silk with both cotton and wool and/or true silk, still further more-or-less-contrasting shades with one dye in a single dye bath, are possible.

### *Know Your Union*

It is of course of prime importance that all of the various fibers accompanying the acetate silk be identified, as mentioned in Chapter V under the identification of the rayons, and their previous treatment (such as the mercerization of cotton[d]) be de-

[d] See Chapter VI.

tected, as well as the particular brand of acetate silk used, if possible, before attempting to dye the goods. Perhaps the best and quickest method of detecting the presence of rayon is by means of the microscope. Either a large sample of the goods may be placed upon the stage, or a few of the suspected fibers mounted on a slide by the usual quick process. In this manner cotton, wool, linen and bast fibers can be recognized at a glance, and real silk distinguished from rayon with very little more difficulty.

If a chemical test is desired to confirm the microscopic findings a sample may be boiled with sodium hydroxide solution. This dissolves the animal fibers, true silk, and wool, leaving the vegetable fibers and all of the rayons. The burning test is a quick and convenient method of distinguishing between true silk and rayon. True silk gives the characteristic odor of burning proteins, while the rayons, with the exception of acetate silk, burn very much like cotton. The acetate rayon fuses rather than burns, as described under the burning test for acetate silk, Chapter V.

It has also been stated that if a sample of union goods containing rayon is heated to 200° C. (392° F.) for ten minutes, the rayon will be completely carbonized and may be dusted out of the sample by rubbing, while the natural fibers (cotton, wool and true silk) are unchanged. A complete review of the methods of identifying the different types of rayon is given in Chapter V.

*References*

[1] F. M. Stevenson, *Dyer and Calico Printer* 55, 86-8 (1926).

## CHAPTER XXVI

## THE BASIC DYES ON ACETATE SILK UNIONS

*The Methods of Dyeing Combinations of Acetate Silk with Cotton, Wool, or True Silk with Basic Dyes.*

WHILE the basic dyes are not generally used on the acetate silk of acetate silk unions for multicolor effects, at the present time, due to the superior qualities of some of the special acetate silk dyes, a knowledge of their behavior in this respect may be of value for certain purposes. In this connection the reader should not neglect Chapter X, on the Basic Dyes on Acetate Silk.

In dyeing cotton-acetate silk unions or combinations of acetate silk with other rayons, it is sometimes easy to secure a wide variety of two color effects by using basic dyes on the acetate silk and direct cotton dyes on the cotton or rayon. If Lustron is used, it is especially easy to secure contrasting colors, due to its high affinity for the basic dyes. Sometimes it is possible to use both the basic and direct dyes in the same dye bath, but usually better results are obtained by using separate baths. If only one bath is used, it is generally best to apply the basic dye first, and when it is about exhausted, to add the direct dye to the bath. If solid, instead of contrasting shades are desired on the two fibers, a more careful selection of the dyes must be made and more care used in their application.

In selecting the direct cotton dyes for use upon rayons or cotton-acetate silk unions, care should be taken to select only those dyes which do not stain acetate silk. For this reason only dyes specially prepared for this particular use should be employed, as mentioned in the previous chapter. However, there are now many lines of cotton dyes prepared particularly for use with acetate silk which do not stain it.[a]

In cross-dyeing acetate silk unions containing cotton or rayon, it is important to dye the acetate silk first, or the substantive dyes

[a]See Chapters XXXIII and XXV.

may mordant the basic dyes on the cotton, thereby causing a staining or dyeing of the cotton or rayon, with the basic dyestuff. In applying the basic dyes to acetate silk-cotton or rayon unions at low temperatures, the basic dyes of course stain both fibers, but as the temperature is raised the color feeds onto the acetate silk (Lustron) from the cotton or rayon, until at a sufficiently high temperature, especially in the presence of acetic acid, the other fibers are clear. Sometimes a fairly high temperature is necessary to clear the fibers accompanying the acetate silk, and in this case the better resistance of Lustron to high temperatures is an advantage in its favor. Plenty of salt should be used in cross-dyeing the cotton, so as to avoid bleeding from the basic dyes.

As an illustration of the two color dyeing process on acetate silk-cotton unions, the following formula gives a bright peacock blue color on Celanese, while the cotton is dyed a grey:

| | |
|---|---|
| Capri Blue GON | 1.5 per cent, |
| Acetic or formic acid (100%) | 2 cubic centimeters per liter, and |
| Sodium chloride | 20 per cent. |

Enter the goods at 45° C. (113° F.) and dye at 45 to 80° C. (113 to 176° F.) for about one hour or until the desired shade is obtained. If necessary the cotton may be cleared as in Methods No. 111, No. 112, or No. 113. Then cross-dye the cotton with

| | |
|---|---|
| CR Chlorazol Fast Gray | 0.3 per cent and |
| Sodium chloride | 5.0 per cent. |

Enter cold and dye at 50° C. (122° F.) or below for about three-quarters of an hour.

Where the cotton in the acetate silk union is to be left white, Chase[1] recommends entering the Lustron-cotton union into a cold or lukewarm dye bath containing 5 to 10 per cent of acetic acid, on the weight of goods. The dyestuff, in solution, is then added and the temperature gradually raised to 66 or 77° C. (150 or 170° F.). Salt may also be added as a retarding agent. If the cotton is stained it can usually be cleared by Method No. 111, but Chase recommends the use of lactic acid in place of the acetic acid; or by Method No. 112.

In spite of the comparatively high affinity of the basic dyes for acetate silk, Blackshaw[2] reports that due to the lack of affinity of

acetate silk for the usual basic dye mordant, *i.e.*, tannin and tartar emetic, it is possible to mordant the cotton of Celanese-cotton unions and by applying the basic dyes in the presence of 5 per cent of formic acid, obtain white acetate silk effects with Celanese; but this effect is not possible with Lustron. He states that acetic acid cannot be substituted for the formic acid above. It is very doubtful if this procedure would be as successful on Lustron-cotton unions as in the presence of Celanese, and very probaby the results, as regards the staining of the acetate silk, vary considerably with the particular basic dye used.

*Method No. 86: Dyeing Acetate Silk-Cotton Unions With Basic and Direct Dyes.* Dye the acetate silk with basic dyes in the presence of acetic acid, as in Methods No. 24 or No. 25. Then fill up the cotton with suitable direct cotton dyes in the usual manner in a dye bath containing salt, soap, or Turkey-red oil, and a little soda, if necessary.

*Method No. 87: Dyeing Acetate Silk-Cotton Unions With Basic Dyes Only.* First mordant the cotton of the union with tannin and antimony in the usual manner. In the case of Lustron, both fibers of the mordanted union may then be dyed with suitable basic dyestuffs in one operation.

*Method No. 88: Janus Dyes on Lustron-Cotton Unions.* The Lustron Company states that Lustron-cotton unions may be dyed solid shades by means of the Janus dyes. The affinity of the Janus dyes for cotton varies considerably with the condition of the cotton, *i.e.*, unbleached, bleached, or mercerized. Their affinity for cotton is greatest somewhat below the boil, while their affinity for Lustron increases with the temperature up to the boiling point. In this manner, by properly regulating the temperature of the dye bath, the dyer can control the dyeing so as to obtain either solid or varying shades upon the two fibers. However Hall states that the Janus dyes, as well as the Acridene and Azine dyes, are not fast upon acetate silk. He probably refers particularly to Celanese.

*Method No. 89: Dyeing Acetate Silk—True Silk Unions With Basic and Acid Dyes.* In dyeing acetate silk-real silk unions, using basic dyes for the former and acid dyes for the true silk,

the two dyes can sometimes be applied in a single dye bath, with acetic acid. In using this single bath method, it is of course imperative that dyestuffs be selected which do not react with each other in the dye bath. For this reason it is usually best to use two dye baths, applying the basic dyes as in Methods No. 24 or No. 25, and then dye the true silk with acid dyestuffs in a fresh acetic acid dye bath, by the usual methods. After dyeing, it is usually desirable to give the material a light soaping, as this assists in clearing the colors. The Gyco Neutral and Kaline dyes, described in Chapter XXXIV, may be particularly useful in this way.

*Three Color Combinations*

In dyeing three color combinations, such as acetate silk, viscose and true silk, using basics on the acetate silk, the acetate silk should be dyed first in a slightly acid bath, the viscose second with direct dyes using salt in an alkaline dye bath, followed by acid dyes for the real silk, in the presence of both acetic acid and salt. On account of its higher resistance to alkalies and high temperatures, and its high affinity for basic dyes, Lustron is probably better suited for this class of work than some of the other varieties of acetate silk.

*Method No. 90: Colored Effects on Acetate Silk-Cotton-True Silk Unions.* The acetate silk (Lustron) may be dyed as in Methods No. 24 or No. 25, with acetic acid. If a white true silk effect is desired, clear this fiber in a weak acetic acid bath, as in Method No. 111; wash and rinse in a dilute sodium bicarbonate bath, as in Method No. 113. Then dye the cotton with direct cotton dyes which do not stain real silk, in a bath containing salt, soap, and a little soda, if necessary.

*Method No. 91: Three Color Effects Upon Acetate Silk-Cotton-True Silk Combinations.* Proceed as in Method No. 90 and then dye the true silk as in Method No. 89.

*Method No. 92: Three Color Effects Upon Acetate Silk-Cotton-True Silk Combinations.* Dye the acetate silk (Lustron) and true silk as in Method No. 88. This will give the same or different colors on the acetate silk and true silk, leaving the cotton white or stained, depending upon the particular dyes used. The cotton

may be cleared by Method No. 112, and then dyed the same or a different color by means of a direct cotton dye which does not stain real silk, in the usual manner.

### *Dyeing Acetate Silk-Wool Unions With Basic Dyes*

Acetate silk-wool unions are more difficult to handle in dyeing than acetate silk-cotton or rayon combinations. While it is not difficult to find acid and other wool dyes which do not stain acetate silk, most of the acetate silk dyes and practically all of the basic dyes, stain or dye wool, and in many instances the dyed wool is a different color from that of the acetate silk. Most of the acid dyes which dye acetate silk give different shades on these two fibers. Some basic dyes such as Magenta and Malachite Green give approximately the same shade on acetate silk and wool, but at low temperatures the wool is dyed a deeper shade. Increased acidity, with acetic acid, and higher temperatures tend to feed the basic dye onto the acetate silk.

*Method No. 93: Basic Dyed Acetate Silk-Wool Unions.* The acetate silk (Lustron) may be dyed with basic dyes as in Methods No. 24 or No. 25 with acetic acid and the wool may be dyed with an acid dye in the same or a fresh bath, as in Method No. 89. Many other acetate silk dyes are particularly adapted for dyeing two or more color effects upon acetate silk unions, and these will all be considered later under the other dyes, in their appropriate order.

*Method No. 94: After-treating Lustron.* Always after treating Lustron with an acid solution, such as in applying the basic dyes in an acetic acid bath, it should receive an after-treatment for 15 to 30 minutes in a cold solution containing 0.25 to 1 gram of sodium bicarbonate (baking soda) per gallon of water. The Lustron should then be hydroextracted and dried without rinsing. This insures that no acid remains in the goods. In selecting dyes for use upon Lustron or unions containing it, only those should be used which do not strip or bleed with this aftertreatment.

*References*

[1] W. W. Chase, *Textile World 71,* 557-8 (1927).
[2] H. Blackshaw, *Dyer and Calico Printer 55,* 192-3 (1926).

# CHAPTER XXVII

## THE ACID AND MORDANT TYPE OF DYES ON ACETATE SILK-COTTON UNIONS

It is of course obvious that the acid and certain mordant dyes may have a particular field of usefulness upon acetate silk and wool or true silk unions. As explained in connection with the use of basic dyes upon acetate silk-wool unions, most of the acetate silk dyes stain or dye wool, particularly in this case. However, a given dye does not always give the same shade or even the same color upon both the acetate silk and the accompanying animal fiber. Of course the colors or shades ultimately obtained from any one dye or combination of dyes are entirely dependent upon the composition, concentration, and temperature of the dye bath. There is no difficulty in finding acid and mordant dyes for use upon wool which do not dye the acetate silk, but the dyeing of wool and cotton materials containing acetate silk white effects will be considered later.

In the case of acetate silk-cotton unions, it is obvious that only in a very few cases of "union" dyes would the acid or mordant dye be applicable to the cotton. Where they are to be applied to the acetate silk in these unions, Method No. 25 may be used.[a] The Lustron Company state that Acid Rhodamine 3R, Azo Yellow A5W or Indian Yellow GA, Coomassie Fast Violet 10BP, Chrome Orange R also known as Alizarine Yellow R or Alizarol Orange R, Pontachrome Yellow 3R, Alizarine Yellow 2G or equivalent, Alliance Fast Brown 5G, Terra Cotta RS, Anthracene Browns and Blues, as well as Modern Violet and Violet PPH or Prune Pure, may be used for this purpose. Many of the basic dyes may be used with them; for instance, Alizarine Yellow R and either Victoria Green WB or Methylene Green B, may be applied in the same bath, by Method No. 25 to obtain a light fast green.

[a] Also see Chapter XIII.

When using a basic dye with a mordant dye, it is best not to add any salt to the dye bath until after the basic dye has been exhausted therefrom, unless it is desired to restrain the rate at which the basic dye feeds on the acetate silk, as salt has a marked retarding action on the basic dyes for acetate silk. Possibly a better way would be to apply the basic dye first cold, with or without salt and acetic acid; then when the bath is exhausted, the mordant dye may be added to the dye bath and the dyeing continued to shade. With most of the mordant dyes on acetate silk, a chrome after-treatment is of no particular benefit. The addition of chromium acetate to the dye bath, when applying the Gallocyanines,[b] will improve their fastness to washing. Where the cotton is stained, it may be cleared by Method No. 111 or this treatment may be followed by Method No. 113, Chapter XXXV.

In a few cases solid colors may be obtained on acetate silk-cotton unions, with combinations of acid and direct cotton dyes. For instance, a solid yellow color may be obtained with Fast Yellow 5GW and Citronine Y conc.; a solid brown shade with Alizidine Brown M, Chlorazol Brown M and Chlorazol Brown LF; or a solid blue with Chlorazol Sky Blue GW and Prune Pure. Many of the dyes discussed elsewhere, such as some of the Acetate and Cellutyl dyes, are also members of the acid and mordant classification of dyes and are applicable to the acetate silk of unions containing it. In the case of acetate silk-wool unions, undoubtedly both fibers would be dyed. However, as a class these older dyes of this classification are rapidly being displaced for use on acetate silk by the special new dyes for acetate silk, some of which apparently belong to the acid and mordant group. Also see Method No. 41 of Chapter XIII.

The Setacyl Direct dyes of the Geigy Company are recommended for use on acetate silk-cotton or rayon unions in connection with the Art Silk CW dyes of the same company, to produce multicolor or shot effects at a very low dyeing cost. They withstand cross-dyeing well, with only a slight staining of the cotton, or viscose in some cases.

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[b] See Chapter X.

While the Cellit Fast dyes as a class usually stain cotton, wool, and true silk to some extent and are therefore not so well suited for use where the fiber accompanying the acetate silk is to be dyed in lighter, contrasting shades, they find a certain use where the accompanying fibers are to be dyed in similar or darker shades. Where only light shades are applied to the acetate silk, the cotton or viscose present in unions can usually be cleared up by a soaping as directed under Clearing Unions, Chapter XXXV.

*Method No. 95: The Cellit Dyes on Acetate Silk Cotton Unions.* Where these dyes are to be applied on cotton-acetate silk materials with a colored warp, the warp should be dyed in the hank. In case a black warp is desired, 7.5 per cent of Katigen Deep Black B gives very good results. After weaving, the acetate silk may be dyed as in Method No. 46, then rinsed and washed in a soap bath at 40 to 49° C. (105 to 120° F.). This washing clears the cotton or viscose, which if still in the white state, may then be dyed in a fresh dye bath at 43 to 49° C. (110 to 120° F.), with an addition of about 20 per cent of calcined Glauber's salt.

# CHAPTER XXVIII

## THE SULFUR DYES ON ACETATE SILK-COTTON UNIONS

THE use of the sulfur dyes on acetate silk was mentioned in Chapter XV. Many sulfur dyes, even blacks, may be applied to acetate silk-cotton unions, leaving the acetate silk clean, if applied at low temperatures in short baths containing as little sodium sulfide and alkali as possible to hold the dye in solution. Method No. 96 has been recommended for Lustron-cotton unions. Where the acetate silk of the acetate silk-cotton union is to be dyed with dispersol dyes, it is usually best to dye the acetate silk first and then cross-dye the cotton either in the padder or jig.

*Method No. 96: Sulfur Dyes on the Cotton of Acetate Silk-Cotton Combinations.* For 100 pounds of dye bath, use 1 pound of Sulfogene Carbon Black H, 2 to 2.25 pounds of sodium sulfide crystals, 0.25 pound of sodium carbonate, and 0.25 to 0.5 pound of salt. Dye at about 20° C. (68° F.) or not over 24° C. (75° F.). A full shade is obtained in an hour or an hour and a quarter.

British Patent No. 214,330, January 18, 1923, to the Clayton Aniline Company covers the use of waste sulfite cellulose liquor, or its constituents, which comprise sodium lignin sulfonate, resinous matter, and various sugars, to protect the acetate silk from the saponifying action of sodium sulfide and other alkalies in dye baths. Its use is particularly recommended in applying sulfur dyes to acetate silk-cotton unions where it is desired to leave the acetate silk white.

In this manner 10 parts by weight of the union, containing not more than 10 per cent of acetate silk may be dyed in a 60 to 1 dye bath containing 2 parts of Pyrogene Deep Black A paste, which is equivalent to 1 part of the pure dry dyestuff, 2 parts of sodium sulfide crystals, 0.2 part of sodium carbonate, 6 parts of Glauber's salt and 2 parts of cellulose-sulfite waste liquor of 1.28 specific gravity. The material is entered at 50 to 60° C. (122 to 140° F.),

and after the temperature has been raised to 80° C. (176° F.), it is dyed at this temperature for one-half hour. The material is then well rinsed. Where it is desired to leave the acetate silk white, Pyrogene Green 3G, Pyrogene Deep Black A, and Pyrogene Cutch 2GR are recommended.

According to British Patent No. 238,721, September 19, 1924, to the British Dyestuffs Corporation and H. D. Mudford, the addition of a suitable quantity of an ammonium salt, *e.g.*, ammonium chloride or sulfate, to the ordinary sulfide dye bath considerably reduces its hydrolyzing action on acetate silk. In this way it is possible to dye the cotton in acetate silk-cotton unions in fast heavy shades with sulfide dyes and leave the acetate silk unstained. This patent refers to British Patent No. 19,473, September 5, 1914, to E. Lodge and J. M. Evans, which covers the dyeing of animal fibers, union goods, and rayons with sulfide dyes in the presence of an alkali sulfide and a neutral ammonium salt.

*Method No. 97: Sulfur Dyes on the Cotton of Acetate Silk-Cotton Unions with Ammonium Sulfate.* Two parts of Thional Black GSX conc. are dissolved by boiling with 4 parts of sodium sulfide crystals in 80 parts of water and placed in the dye bath. A solution of 2 parts of ammonium sulfate in 20 parts of water is then added and the scoured, thoroughly wet-out goods entered. The dyeing is carried out at 80 to 85° C. (176 to 185° F.), after which the material is thoroughly rinsed with hot water until free of alkali and adhering dyestuff. Thional Black OG, Liquid Sulfur Blacks G, L and R, Thional Browns P and B, Thional Corinth GX, and Thional Greens B and 2G, may also be used in the same way.

Possibly the patent of F. L. Remlin and the Du Pont de Nemours Company, United States Patent No. 1,551,330, August 25, 1925, may also be useful in applying the sulfur dyes to unions containing acetate silk. This patent covers the application of sulfur dyes to real silk in dye baths of reduced alkalinity, by the addition of sodium hydrosulfite, sodium bisulfite, and 0.75 to 5.0 per cent, on the weight of the dye bath, of a "gum soap." Method No. 98 covers the use of a special "Reserve Salt."

*Method No. 98: Kryogene Black TBOC on Cotton-Acetate Silk*

*Unions.* Prepare the dye bath with 6 grams of Kryogene Black TBOC, 16 grams of sodium sulfide crystals, 2.5 grams of calcined soda, 30 grams of calcined Glauber's salt, and 60 grams of Reserve for Acetate Silk, per liter of liquor. Dye at 40 to 50° C. (104 to 122° F.) for an hour. Squeeze direct from the dye bath and rinse thoroughly at once. The white effect is improved by a subsequent soaping at 50 to 60° C. (122 to 140° F.) in a bath containing 5 grams of olive oil soap per liter. When a standing bath is used, cut the sulfide to a half or a third of the amount used in starting. and add the Reserve Salt and Glauber's Salt according to the volume of liquor removed from the dye bath.

Besides the sulfite cellulose waste liquor (Protectol) and ammonium sulfate which have been mentioned as protective agents in the application of the sulfur dyes to acetate silk-cotton unions, casein, glucose and cresolsulfonic acid, etc., have also been mentioned, but do not appear to have found much use in commercial practice. Sodium phenolate has been recommended as a leveling agent for these, as well as other dyes, in an alkaline dye bath.

# CHAPTER XXIX

## THE VAT DYES ON THE COTTON OF ACETATE SILK-COTTON UNIONS

WHERE very fast-to-light dyes, such as most of the dispersol products, are used on the acetate silk of acetate silk-cotton unions, in order to obtain a correspondingly fast color on the cotton, it is necessary to dye it only with vat dyes. On account of the sensitiveness of acetate silk to alkalies and the necessity of using a more or less alkaline dye bath in the application of the vat dyes to all textile fibers, at first thought it might appear to be an impossibility; but as usual, the difficulties have been overcome to a large extent, and a selected list of suitable vat dyes may now be applied to cotton, in the presence of acetate silk, by methods somewhat similar to those used in vat-dyeing wool or silk.

In applying the vat dyes to the cotton of acetate silk-cotton unions, it is, of course, necessary first to scour the union by the method generally recommended for the particular type of acetate silk used in the union. It may then be bleached by either the hypochlorite or peroxide method, as described under bleaching,[a] and if hypochlorite was used is given the usual antichlor treatment.

In the application of the vat dyes to acetate silk-cotton unions, only the two-bath method is used, owing to the fact that the color of many of the dispersol colors on acetate silk is altered on cross-dyeing the cotton in a hydrosulfite dye bath. According to the dyeing methods of the manufacturers of Celanese, the vat dyes suitable for application to cotton by their methods, may also be applied to wool and true silk. Probably in many cases the methods previously proposed by Scottish dyes may also be applicable to vat-dyeing wool and true silk, either alone or in combination with acetate silk. According to British Patent No. 214,112, as well as many other patents mentioned in connection with the vat dyes on

[a]See Chapter IX.

acetate silk,[b] certain vat dyes may also be applied to acetate silk from a hydrosulfite vat, in which case it may be possible to dye acetate silk unions in a single hydrosulfite dye bath. Undoubtedly the Ciba dyes may be applied to both fibers of acetate silk-cotton unions by Method No. 54.

*Caldeon Vat Dyes on the Cotton or Viscose of Acetate Silk Unions*

The cotton or viscose silk is always dyed before the acetate silk and the methods used are similar to those normally adopted in dyeing cotton except for certain modifications which have to be introduced to avoid any deterioration in the acetate silk. As the acetate silk is easily hydrolyzed by caustic alkalies, the vat-dyeing operation must be carried out at about 25° C. (77° F.). The cold dyeing Caledon dyestuffs are consequently the most suitable. Most of the hot or medium dyeing dyestuffs, however, may be used although some loss of dyestuff must be expected with these latter. It is not generally advisable to dye in deeper shades than 10 per cent as it is difficult to obtain these economically without staining the acetate silk. The methods to be used with the various Caledon dyes can be seen from Table LVI.

TABLE LVI

VATTING TEMPERATURES FOR THE CALEDON DYES

| | *Vatting Temp. °F.* | *Group* | | *Vatting Temp. °F.* | *Group* |
|---|---|---|---|---|---|
| Cal. Blue GC. | 120 | 1 | Cal. Green B. | 140 | 1 |
| Cal. Blue GCD. | 120 | 1 | Cal. Gold Orange G. | 140 | 1 |
| Cal. Blue GCP. | 120 | 1 | Cal. Jade Green | 110 | 1 |
| Cal. Blue R. | 140 | 1 | Cal. Orange RRT. | 140 | 1 |
| Cal. Blue RC. | 120 | 1 | Cal. Purple R. | 140 | 1 |
| Cal. Blue RR. | 120 | 1 | Cal. Red BN. | 80–100 | 2 |
| Cal. Brill. Blue R. | 140 | 1 | Cal. Red FF. | 120 | 3 |
| Cal. Brill. Purple RR. | 140 | 1 | Cal. Red 5B. | 120 | 3 |
| Cal. Brill. Violet R. | 105 | 3 | Cal. Red Violet 2 RN. | 80–100 | 2 |
| Cal. Brown B. | 140 | 1 | Cal. Violet RN. | 120 | 2 |
| Cal. Brown G. | 120 | 3 | Cal. Yellow G. | 140 | 1 |
| Cal. Brown KT. | 80–100 | 2 | Cal. Yellow 3G. | 105 | 3 |
| Cal. Brown R. | 105 | 3 | | | |
| Cal. Dark Blue B. | 140 | 1 | | | |

[b]Chapter XV.

When the material is to be dyed in the form of *cops, cheeses, beam-warps,* or in the piece, the composition of the dye bath for 100 pounds of material, *i.e.,* for material containing 100 pounds cotton, can be read off from Table LVII.

TABLE LVII

COMPOSITION OF THE DYE BATH FOR THE CALEDON DYES IN MACHINES

| | *Group 1* | *Group 2* | *Group 3* |
|---|---|---|---|
| Water (British Gallons) | 50–80 | 50–80 | 50–80 |
| Caustic soda solution 53°Tw. (pints) | 7–9 | 3.5–4.5 | 5.9 |
| Caustic soda solution 73°Tw. (pints) | 5–7 | 2.5–3 | 3.5–4.5 |
| Hydrosulfite conc. powder (pounds) | 1.5–2.5 | 1.5–2.5 | 1–2.5 |
| Glaubers Salt Crystalline (pounds) | | 10.–20 | 2.5–10 |

*Method No. 99: The Caledon Dyes on Acetate Silk Unions by Machine.* After the material has been well wet-out at a temperature not exceeding 79° C. (170° F.), the machine is filled with the softest water obtainable, one-third of the above quantities of caustic and hydrosulfite added, and the machine run for a short time. In the meantime the dyestuff is dissolved separately. The paste is stirred with about ten times its quantity of water, the remainder of the caustic and hydrosulfite added, the temperature raised to that given in Table LVI for vatting, and this liquor, when the dyestuff is in solution, is passed into the dye bath through a fine sieve.

In the case of yarn dyeing, after the liquor has been run off or the yarn lifted, it is of advantage to see that the liquor still in the yarn is quickly removed, *e.g.,* with compressed air, or better, with a vacuum pump. When dyeing beam-warps with Caledon colors requiring an addition of salt, this should not exceed 7 pounds per 100 gallons of dye bath.

*Method No. 100: The Caledon Dyes on Acetate Silk Union Yarns in the Open Beck.* The dye vat is prepared with about 180 gallons of water, 1 to 2 pints of 53° Tw. caustic soda solution, and 0.5 to 1 pound of hydrosulfite concentrated powder. The dye bath is then heated to the temperature given in Table LVI. The dyestuff is dissolved in 15 or 20 gallons of water with the remainder of the caustic solution, hydrosulfite, etc., as shown in Table LVIII. The dyeing is carried out cold.

TABLE LVIII

COMPOSITION OF THE DYE BATH FOR THE CALEDON DYES IN THE OPEN BECK

| | *Group 1* | *Group 2* | *Group 3* |
|---|---|---|---|
| Water (British gallons) | 200 | 200 | 200 |
| Caustic soda solution 53°Tw. (gallons) | 2 | 1 | 0.2–0.6[c] |
| Hydrosulfite Concentrated Powder (lbs.) | 2–2.25 | 2.25–2.5 | 1–4 |
| Glauber's salt crystals (lbs.) | | 10–40 | 10–80 |

[c]Caldeon Brilliant Violet R requires 33 per cent more caustic soda solution than the amount given above.

After dyeing, the material is wrung and allowed to oxidize for 20 minutes. It is then rinsed absolutely free from alkali as this may hinder the exhaustion of the Celatene dyes. If necessary a small amount of acid may be used for this purpose. This acid does not interfere with the dyeing of the Celatene dyestuffs. When free from alkali the goods are dyed by the methods given for the Celatene dyes on acetate silk, Chapter XXII.

After exhaustion has taken place the goods are withdrawn from the dye bath, wrung lightly and soaped for 15 minutes in a 60° C. (140° F.) soap bath containing 10 pounds soap per 100 British gallons. This soaping serves a triple purpose, and is essential for bright, clean-cut effects.

(*a*) It clears the viscose of a certain amount of superficial, loosely attached Celatene dye.

(*b*) It clears the acetate silk of a certain amount of superficial, loosely attached vat dye.

(*c*) It brightens both the vat color on the viscose and the Celatene color on the acetate silk.

After soaping, the goods are washed free from soap (given a slight sour in the case of Caledon Red FF, Celatene Fast Light Brown, Celatene Fast Light Yellow and Celatene Gold Orange), wrung lightly, and dried.

*The Anthrene and Thianthrene Dyes*

Certain Anthrene and Thianthrene dyes of the Newport Chemical Works have also been recommended for use upon the cotton of acetate silk-cotton unions, especially in combination with the

Celanthrene dyes of the same company. The Anthrene dyes are very similar to the Caledon dyes mentioned above and undoubtedly they may be applied by the methods given for the Caledon dyes. On account of the restrictions imposed by the presence of acetate silk, the following vat dyestuffs have been selected as the most suitable for this purpose; however, others may be used with the proper methods and care:

| | |
|---|---|
| Anthrene Red 3BN paste | Anthrene Golden Orange RRT paste |
| Anthrene Violet BNX paste | Anthrene Golden Orange G paste |
| Anthrene Brown BB paste | Anthrene Violet 2R paste |
| Anthrene Jade Green paste | Thianthrene Pink FF paste |
| Anthrene Blue GCD paste | Thianthrene Orange R paste |

The cotton should of course be dyed first at as low a temperature and alkalinity as possible. Obviously, considerably more care must be used in the application of heavy shades than for tints, and some loss of vat dyestuff may be expected. After the oxidation of the vat color, all traces of alkali should be removed from the goods by rinsing them in a dilute organic acid bath. The acetate silk can then be cross-dyed with Celanthrene dyestuffs, as given in Chapter XXII. The entire piece can be finished by soaping in the usual manner for the development of vat colors.

### *Vat Dyes on Celanese-Cotton Unions*

The manufacturers of Celanese[5] have obtained patents upon a special method of applying certain vat dyes to cotton, as well as other materials, containing Celanese. This method involves the use of the alkali salts of phenolic bodies, such as sodium phenolate, naphtholate, resorcinate, cresolate, etc., and is based upon the fact that Celanese is not saponified by these compounds in the concentration required in the dyeing at temperatures below about 60° C. (140° F.). The process is protected by patent and may be used only on materials containing the Celanese brand of acetate silk. The following dyes have been recommended[1, 4, and 5] for use by this method:

| | |
|---|---|
| Caldeon Red BN | Eridan Scarlet R |
| Indanthrene Red BK, RK, and 5GK | Eridan Brilliant Scarlet B |
| Anthrene Red BN | Indanthrene Pink B |

Indanthrene Orange 3R
Anthrene Golden Orange RRT
Indanthrene Golden Orange 3G
Indanthrene Yellow RK and FFRK
Cibanone Yellow R
Hydron Yellow 2G
Anthrene Jade Green
Anthrene Green B
Ponsol Green BN
Caldeon Jade Green
Algol Blue K
Ponsol Blue 3G
Duranthrene Blue 3GT
Sulphanthrene Blue GR
Indanthrene Blue 3G
Hydron Blue G
Indanthrene Brilliant Violet 2R, 4R, RK, and 2BK
Newport Violet 2R
Ponsol Violet RRD
Indanthrene Violet B and BN
Duranthrene Red Violet 2RN
Indanthrene Reddish-Violet RRK
Anthrene Brown BB
Indanthrene Brown R and 3R
Algol Brown G and R
Indanthrene Gray 3B, 6B, BTR, and RRH
Ponsol Black B double
Anthrene Black BB
Indanthrene Black 2B
Caledon Black B

All of the above dyes leave Celanese practically unstained.[4] While Indanthrene Blues R and GC are not applicable by the phenolate method, good results are obtained with the methyl derivative formerly known as Algol Blue K and the Hydron Blues. In selecting vat dyes for use on the cotton of Celanese white or two-color effects, two factors are involved: (*a*) the dye must be applicable by the phenolate process, and (*b*) it must resist the acetate silk. Where a uniform color on both fibers is desired, *b* is of course of less importance. Undoubtedly other vat dyes than those mentioned in the list are useful by this method. Some Indigoid vat dyes dye Celanese fairly well[4] but are not generally fast to rubbing.

For economic reasons, sodium phenolate is the only one of the salts mentioned that is used in the commercial application of vat dyes by this method. This salt, especially in the presence of an amphoteric colloid such as glue, has much less hydrolyzing action on the acetate silk as well as on wool and silk, than a corresponding amount of caustic alkali. As in the application of the Caledon dyes to acetate silk unions, the cotton or viscose is dyed first and then the acetate silk cross-dyed with the S. R. A. dyes by the methods previously given in Chapter XXI.

In practice, the vat dye bath is prepared in exactly the same manner as for the application of the same dye to cotton or viscose

alone, except that sodium phenolate is substituted for the caustic alkali. Or, if it is preferred, the vat dyes may be vatted in the usual manner with sodium hydroxide and then the vat neutralized with phenol or a related compound. However, this latter method requires very careful chemical control. As is well known, each individual vat dye differs from the others regarding the amount of sodium hydroxide and hydrosulfite required, and therefore only a general formula is possible here.

*Method No. 101: The Vat Dyes on Celanese-Cotton Unions.* In preparing the "stock vat," the vat dye paste, in quantity equivalent to 100 grams of the powder, is mixed with 10 liters of hot water of such a temperature as to give a final temperature of 50° C. (122° F.) in the stock vat; 3 kilos of sodium phenolate are added, and then about 300 grams of sodium hydrosulfite are sifted in while stirring well, until properly reduced. When the vat dye in powder form is used, the powder should first be pasted with Turkey-red oil before mixing it with the water.

The 20 to 1 dye bath is prepared by adding for each 100 liters of bath, 60 grams of sodium phenolate, 15 grams of hydrosulfite, and 35 grams of glue, previously dissolved in water. An appropriate quantity of the stock vat solution is then added.

Where it is desired to prepare the dye bath directly without the use of a stock vat, the vat dye powder is pasted with a little Turkey-red oil and added directly to the 50° C. (122° F.) dye bath, which has previously been prepared by adding to each 100 liters of solution, 1.5 kilos of sodium phenolate and 35 grams of glue, previously dissolved in water. The necessary quantity of sodium hydrosulfite is then dredged in and the bath gently stirred. After about 15 minutes, when the reduction is complete, the dyeing may proceed as usual.

The goods are entered and dyed at 40 to 50° C. (104 to 122° F.). When properly conducted the Celanese should be practically unstained if a suitable vat dye has been selected; however, some vat dyes stain Celanese. After dyeing, the goods should be squeezed, oxidized, rinsed in soft water containing 0.2 grams of hydrosulfite per liter, and finally rinsed well in pure water. The material is then ready for cross-dyeing the acetate silk with the

S.R.A. dyes by the methods given in Chapter XXI. While the sodium phenolate vat dye solution does not readily attack Celanese, in dyeing it is advisable not to use a temperature above 60° C. (140° F.), instead of 75 or 80° C. as in the application of other dyes in a less alkaline solution.

In using *B*-naphthol in the application of the vat dyes to the cotton of acetate silk-cotton unions, the following formulas have been suggested.[6]

4 to 8 pints of 76° Tw. (1.380 sp. gr.) sodium hydroxide solution,
1.75 to 3.5 pounds of *B*-naphthol, and
1.5 to 4 pounds of hydrosulfite powder.

Half of this caustic soda is used to dissolve the *B*-naphthol in the usual manner, by pasting and pouring on hot water. The dyestuff is reduced in a separate vessel as follows:

1 pound of vat dye in paste,
2 gallons of water at 50 to 55° C. (120 to 130° F.),
0.5 pint of 76° Tw. sodium hydroxide solution, and
4 ounces of hydrosulfite powder.

Any caustic soda or hydrosulfite remaining from the upper formula is added to the dye bath, followed by the *B*-naphthol solution, and then the reduced dyestuff solution, after 15 to 20 minutes reduction. The dyed material is oxidized in the usual manner and then soaped at 70 to 80° C. (160 to 175° F.). The following dyestuffs have been recommended as applicable by this process.

Duranthrene Yellow G Extra
Duranthrene Golden Orange Y and 2RT
Duranthrene Red 5G and BN
Duranthrene Red Violet 2RN
Duranthrene Brilliant Violet R
Duranthrene Green 2B
Duranthrene Blue GCD
Duranthrene Olive R
Duranthrene Violet 2R

As the following S.R.A. dyes are particularly fast to light, they are recommended[5] as very suitable for use on acetate silk unions containing vat-dyed cotton or viscose:

S.R.A. Golden Yellow X
S.R.A. Golden Orange I
S.R.A. Golden Orange III
S.R.A. Red VII
S.R.A. Heliotrope I
S.R.A. Violet II
S.R.A. Blue III
S.R.A. Blue IV
S.R.A. Black IV, developed with BON

By this method a wide variety of very fast-to-light solid or contrasting shades may be obtained on acetate silk-cotton or -viscose unions, using dyestuff combinations of which the following serve as examples:

No. V-1: Solid Bright Saxe
10% Ponsol Blue 3G paste and
0.4% S.R.A. Blue IV paste.

No. V-2: Solid Rose
10% Anthrene Red BN paste,
2% S.R.A. Red VII paste, and
1% S.R.A. Golden Yellow X paste.

No. V-3: Solid Violet
5% Anthrene Violet 2R paste,
1.5% S.R.A. Violet II paste, and
0.8% S.R.A. Heliotrope I paste.

No. V-4: Cotton Saxe, Celanese Orange
10% Ponsol Blue 3G paste,
10% S.R.A. Golden Orange III paste, and
2% S.R.A. Red VII paste.

No. V-5: Cotton Green, Celanese Heliotrope
5% Anthrene Jade Green paste, and
2% S.R.A. Heliotrope paste.

No. V-6: Cotton Rose, Celanese Blue
10% Anthrene Red BN paste and
2% S.R.A. Blue III paste.

No. V-7: Cotton Brownish-Orange, Celanese Saxe
10% Anthrene Golden Orange RRT paste and
2% S.R.A. Blue IV paste.

No. V-8: Cotton Gray, Celanese Green
10% Anthrene Black BB paste (after-treated with hypochlorite)
1% S.R.A. Blue IV paste, and
0.7% S.R.A. Golden Yellow X paste.

No. V-9: Cotton Violet, Celanese Golden Orange
5% Ponsol Violet RRD paste and
2% S.R.A. Golden Orange I paste.

No. V-10: Cotton Brown, Celanese Violet
18% Anthrene Brown BB paste and
2% S.R.A. Violet II paste.

No. V-11 Cotton Saxe, Celanese Red
7.5% Ponsol Blue 3G paste,
2.5% S.R.A. Golden Orange III paste, and
1.5% S.R.A. Red VII paste.

No. V-12: Cotton Green, Celanese Gold
5% Anthrene Jade Green paste and
2% S.R.A. Golden Orange III paste.

No. V-13: Cotton Blue, Celanese Heliotrope
10% Ponsol Blue 3G paste and
1% S.R.A. Heliotrope I paste.

No. V-14: Cotton Green, Celanese Red
5% Anthrene Jade Green paste and
2% S.R.A. Red VII paste.

No. V-15: Cotton Green, Celanese Light Brown
5% Anthrene Green Double B paste,
2.5% S.R.A. Golden Orange I paste, and
0.7% S.R.A. Violet II paste.

No. V-16: Cotton Dark Blue, Celanese Cherry Red
5% Sulfanthrene Blue BR paste and
5% S.R.A. Red VII paste.

No. V-17 Cotton Drab, Celanese Saxe
1% Anthrene Brown BB paste and
2% S.R.A. Blue IV paste.

No. V-18: Cotton Violet, Celanese Gold
5% Anthrene Violet 2R paste and
10% S.R.A. Golden Yellow X paste.

It is understood that this process is being widely used in England with most excellent results.

Very probably some of the protective agents recommended for use in connection with the sulfur dyes on acetate silk-cotton dyes, such as sulfite cellulose liquor (Protectol), ammonium chloride or sulfate, glucose, cresolsulfonic acid, casein, etc., may also be of some value in the application of vat dyes to acetate silk.

Also see British Patent No. 262,506.

### *The New Soluble Vat Dyes*

The new "soluble vat" dyes, such as the Indigosols and Soledons offer interesting possibilities for use on acetate silk unions for

very fast shades on the cotton and wool. They are applied to cotton in a neutral dye bath, or to wool in about the same manner as the ordinary acid dye, and then oxidized on the fiber. A constantly increasing variety of colors are becoming available in this form, and while most of them do not have much affinity for acetate silk, they offer certain advantages for very fast prints, etc., on acetate silk-cotton or wool unions.[3]

*References*

[1] F. M. Stevenson, *Dyer and Calico Printer 55,* 86-8 (1926).
[2] R. G. Dort, *Chemicals 25,* No. 1, 22 (1926).
[3] C. E. Mullin, *Textile Colorist,* January, February and September (1925).
[4] G. H. Ellis, *J. Soc. Dyers and Colourists 42,* 184-6 (1926).
[5] American Cellulose and Chemical Co. "Celanese Dyeing Leaflet No. 5," 1st Edition (April, 1926).
[6] British Dyestuffs Corporation, "Dyeing and Printing Artificial Silk" 1926).

# CHAPTER XXX

## THE DEVELOPED COLORS ON ACETATE SILK UNIONS

As previously mentioned in connection with the production of the azoic or developed colors on acetate silk, most of the developed color components which are applicable to acetate silk alone are also applicable to acetate silk-cotton combinations, many of them leaving the cotton white, while others stain it more or less. Considerable information along this line was given in connection with the discussion of the various brands of these products on acetate silk in Chapter XVI. In the same way, in dyeing the cotton of acetate silk-cotton unions, such as hosiery, with developed colors, a number of products are applicable, many of which do not dye the acetate silk; but quite a few of them stain it somewhat.

In this connection, the difference in the order in which the developed or azo dye components are applied to cotton and acetate silk should be noted. In applying the developed colors on cotton, the fiber is usually first padded in the naphthol bath and then the color developed in a second bath containing the diazotized amino base. In obtaining these colors on acetate silk, just the reverse of this order is used. The acetate silk is first treated with the amino base, for which it has a decided affinity. This is diazotized on the fiber and then developed in the naphthol or phenolic bath, the acetate silk having much less affinity for this latter component than for the amino compound.

In dyeing the cotton of acetate silk with developed colors, where it is desired to leave the acetate silk unstained, only naphthol AS should be used in developing the cotton, as *B*-naphthol and the diamines have an affinity for the acetate silk and usually stain it pink or brownish. Method No. 102, covering the application of the Azoniles to the acetate silk of acetate silk-cotton unions, is an example of the procedure used in this class of work. The S.R.A. Diazo Solamines were at one time recommended for this work,

especially for fast heavy shades on acetate silk-cotton hosiery; but they have since been withdrawn from the market, except for blacks, as the dispersol type of dyes are much easier to apply and in many instances are just as satisfactory with regard to fastness. While Method No. 102 covers the Azoniles, most of the other brands of these dyes may be applied to acetate silk-cotton unions by the process given in Methods No. 61 to No. 68-B in Chapter XVI.

*Method No. 102: The Azoniles on Acetate Silk-Cotton Unions.* The well-scoured and thoroughly wet-out union is entered into a 40 to 1 dye bath containing the Azonile dye at 40 to 49° C. (105 to 120° F.). The temperature is raised to about 74° C. (165° F.) for a half to three-quarters of an hour, and 10 to 20 per cent of ammonium acetate is added. After dyeing, the goods are rinsed in luke-warm water, diazotized as in Method No. 63-A, and developed with a suitable developer as in Method No. 63-B. The cotton may be dyed in a fresh bath. Where the cotton is to be dyed with substantive dyes, it is usually best to dye the acetate silk first according to a process similar to Method 102 and then after diazotizing and developing, dye the cotton with such substantive dyes as do not stain acetate silk at 40 to 60° C. (104 to 140° F.), or at a maximum of 80° C. (176° F.).

It may be mentioned that Cellutyl Union Blacks R and G are mixtures prepared especially to give a solid black color on acetate silk-cotton hoisery.. They are diazotized and developed with *B*-hydroxynaphthoic acid. The dye bath is prepared with 10 per cent of dyestuff, 2 per cent of sodium carbonate, and 10 to 20 per cent of sodium chloride. The goods are entered and the temperature quickly raised to 80° C. (175° F.), for about an hour, further additions of 30 per cent of salt being made. The ratio of dye bath to stock should be kept as low as possible.

The dyed material is rinsed and diazotized for 20 minutes in a cold bath containing 2.5 per cent of sodium nitrite and 7.5 per cent of 32° Tw. hydrochloric acid.

The material is then rinsed and developed for 30 minutes at 50° C. (120° F.) in a bath containing 5 per cent of *B*-hydroxynaphthoic acid, acidulated with acetic acid. The goods are finally

rinsed and soaped for 20 minutes at 50° C. (120° F.) in a bath containing 2 pounds of soap per 100 gallons of water.

The S.R.A. Blacks III and IV really belong to the developed class as they are diazotized and developed on the fiber. In fact, the most satisfactory blacks for acetate silk available today belong to the developed class of dyes. While the Ionamines are a special class of dyes produced particularly for acetate silk, most of them really belong in the developed color class. In the discussion of the developed colors in Chapter XVI, many references were made to developed colors on acetate silk similar to those used on cotton, such as Para-red, Primuline, etc. No doubt many of these processes may be operated so as to dye both the acetate silk and the cotton.

A. E. Hunter, in British Patent No. 191,120 of 1921, states that fabrics composed of viscose or other rayons in combination with acetate silk may be dyed in contrasting shades from a bath containing an excess of sodium carbonate or other suitable alkali, by using a dye containing one or more amino, alkylamino, or arylamino groups, *i.e.*, a dye capable of forming salts with acids, for coloring the acetate silk, and previously, simultaneously, or subsequently dyeing the viscose rayon another shade by means of a direct cotton dyestuff.

## CHAPTER XXXI

## THE IONAMINES ON ACETATE SILK COTTON UNIONS

THE fact that the Ionamines have no affinity for cotton or the older rayons renders them particularly useful in dyeing white cotton or two-colored affects on acetate silk material. As they may be applied in a dye bath slightly alkaline with sodium carbonate and are not affected by the presence of salt, these effects as well as solid colors on acetate silk-cotton unions, may frequently be obtained in one dye bath. Where two-colored effects are desired, it is usually best to cross-dye the cotton, in order to match the shades with those of the sample.

In this manner a deep solid black, suitable for hosiery, etc., is obtained from a single dye bath containing a suitable diazotizable cotton black and Ionamine A. Cellutyl Union Black R is probably such a combination. The dyeing is carried out in a slightly alkaline bath at 75° C. (167° F.) with the addition of 20 per cent of salt. The goods are then diazotized and developed with *B*-hydroxynaphthoic acid. Or the acetate silk may be dyed with the Ionamine A from a slightly acid bath, which is then rendered alkaline with sodium carbonate and the cotton dye added.

As examples of the combinations possible, a bright orange shade on acetate silk and a blue shade on the cotton may be obtained by means of Ionamine B and Chlorazol Sky Blue 2F, without subsequent development. A blue shade on the acetate silk and a bluish-red on the cotton may be obtained by dyeing with Primuline and Ionamine L in a slightly alkaline bath and developing with *B*-hydroxynaphthoic acid. A solid shade of red on acetate silk-cotton unions may be obtained directly with Ionamine Red KA and Chlorazol Fast Red K.

## CHAPTER XXXII

## THE DISPERSOL DYES ON ACETATE SILK-COTTON UNIONS

On account of the excellent fastness properties of many of the dispersol dyes, the large variety of colors available, their ease of application, and the fact that they may be applied in the same dye bath with dyes of other classes, particularly the direct cotton dyes, to leave cotton unstained, they offer extremely interesting possibilities for, and are at present very widely used on, acetate silk-cotton unions, both for cotton-white and two-color effects. As mentioned in connection with the use of the vat dyes on the cotton of these unions, they offer a very simple and convenient method for obtaining shades on acetate silk of a fastness approaching that of the vat dyes on cotton. While some of the developed colors also have excellent and, in some cases, even superior fastness properties to some factors on acetate silk, their longer and more involved methods of application frequently preclude their use.

In cross-dyeing fabrics containing Celanese,[1] where it is desired to leave the accompanying fibers (cotton or other rayons) unstained, it is necessary to use a minimum amount of the dispersol dyestuff to bring the Celanese to shade. If deep shades are desired on the Celanese, it is best to add the dispersol dyestuff in portions, so that it will not flash onto the cotton or older rayon mechanically. The presence of from 0.5 to 1.5 gram of olive oil soap and 1 to 3 cubic centimeters of Turkey-red oil or Celascour per liter of dye bath, is also an aid in leaving the other fibers unstained. The goods should be entered at about 71° C. (160° F.) and the temperature raised immediately to 76° C. (170° F.) at which they should be dyed. In this way clearer cotton whites are obtained than from a cold dye bath.

If for any reason it is desired to enter the union into a cold dye bath, this may be done, and the temperature gradually raised to 75° or 80° C. (167 or 176° F.). In either case the dye bath should not contain more than half of the direct cotton dye and preferably

not all of the dispersol dyestuff, if white or contrasting cotton effects are desired. Where solid shades are being applied on both fibers, less care can be given to the staining. If the dispersol dye was not all added to the bath at the start, it is best to complete the addition of this dyestuff before adding the rest of the direct cotton dye, which is then added in portions as required, the salt being added in the final stage to aid the exhaustion of the direct dye. The dyeing is usually complete in an hour or two at from 60 to 80° C. (140 to 176° F.). After dyeing, the material should be given a light soaping for 10 minutes in a bath containing about 1.5 grams per liter of olive oil soap at 45° C. (113° F.). Slightly stained whites may be cleared as directed in Chapter XXXV.

### *Solid Shades on Acetate Silk-Cotton Unions*

The following formulas[4] will serve as examples of those used in obtaining solid shades on unions of Celanese with cotton or the older rayons:

#### *Formulae*

No. U-1: Light Gray
- 1.0% S.R.A. Blue III paste,
- 0.25% S.R.A. Golden Yellow IX paste,
- 0.08% S.R.A. Orange I paste,
- 0.3% C.R. Cotton Fast Gray B and
- 10.0% Glauber's salt.

Enter cold and raise to 80° C. (176° F.) in 45 minutes. Dye at this temperature for 45 minutes.

No. U-2: Pale Gold
- 1.0% S.R.A. Golden Yellow IX paste,
- 0.2% S.R.A. Heliotrope I paste,
- 0.005% C.R. Cotton Fast Yellow B, and
- 0.04% C.R. Cotton Fast Brown R.

Enter cold and raise to 70° C. (158° F.) for about 2 hours.

No. U-3: Fawn
- 0.4% S.R.A. Blue III paste,
- 0.65% S.R.A. Golden Yellow IX paste,
- 0.04% S.R.A. Red I paste,
- 0.05% C.R. Cotton Fast Brown R,
- 0.04% Chlorazol Fast Yellow B, and
- 5.0% Glauber's salt.

Enter cold and raise to 75° C. (167° F.) in an hour and a half.

No. U-4: Tangarine
3.5% S.R.A. Golden Yellow IX paste,
2.75% S.R.A. Red I paste,
1.3% C.R. Cotton Fast Scarlet 4BS,
1.3% C.R. Cotton Fast Yellow B, and
10.0% Glauber's salt.
Enter cold and raise to 80° C. (176° F.) in 45 minutes, and hold at this temperature for 45 minutes.

No. U-5: Apple Green
0.95% S.R.A. Pure Yellow II paste,
0.12% S.R.A. Blue IV paste,
0.05% C.R. Cotton Fast Blue FF,
0.125% C.R. Cotton Fast Yellow A, and
10.0% Glauber's salt.
Enter cold and raise to 75° C. (167° F.) in an hour.

No. U-6: Light Blue
2.5% S.R.A. Blue IV paste,
0.75% C.R. Cotton Blue FF, and
10.0% Glauber's salt.
Enter cold and raise to 75° C. (167° F.) in an hour and a half.

No. U-7: Dark Beaver
1.4% S.R.A. Blue III paste,
4.6% S.R.A. Golden Yellow VIII paste,
0.3% S.R.A. Red I paste,
2.0% C.R. Cotton Fast Brown R, and
0.2% C.R. Cotton Fast Blue FF.
Enter cold and raise to 80° C. (176° F.) in 45 minutes and dye at this temperature for 45 minutes.

No. U-8: Putty
0.4% S.R.A. Blue III paste,
0.5% S.R.A. Golden Yellow IX paste,
0.06% S.R.A. Heliotrope I paste,
0.015% C.R. Cotton Fast Gray B,
0.003% C.R. Cotton Fast Brown R,
0.001% C.R. Cotton Fast Yellow B, and
5.0% Glauber's salt.

No. U-9: Flesh
0.15% S.R.A. Orange I paste,
0.0072% C.R. Cotton Fast Brown R, and
0.004% C.R. Cotton Fast Scarlet 4BS.

No. U-10: Mushroom
0.3% S.R.A. Blue III paste,
0.1% S.R.A. Golden Yellow IX paste,
0.01% S.R.A. Red I paste,
0.01% C.R. Cotton Fast Gray B,
0.003% C.R. Cotton Fast Yellow B,
0.001% C.R. Cotton Chlorazol Fast Red BL, and
5.0% Glauber's salt.

No. U-11: Nigger
15.0% S.R.A. Blue III paste,
10.0% S.R.A. Golden Yellow VIII paste,
0.5% S.R.A. Red I paste,
4.0% C.R. Cotton Fast Brown R,
0.3% C.R. Cotton Fast Blue FFB, and
20.0% Glauber's salt.

No. U-12: Scarlet
5.0% S.R.A. Red I paste,
1.25% C.R. Cotton Fast Scarlet 4BS, and
15.0% Glauber's salt.
Enter cold and dye at 75° C. (167° F.) for an hour and a half.

No. U-13: Maize
3.2% S.R.A. Golden Yellow IX paste,
0.12 S.R.A. Orange I paste,
0.5% C.R. Cotton Fast Yellow B,
0.16% C.R. Cotton Fast Orange 5R, and
0.04% C.R. Cotton Fast Blue FFB.

No. U-14: Navy
25.0% S.R.A. Blue III paste,
4.0% S.R.A. Golden Yellow IX paste,
4.0% S.R.A. Orange II paste,
2.5% C.R. Cotton Diazo Black BH, and
20.0% Glauber's salt.

No. U-15: Light Brown
5.0% S.R.A. Orange II paste,
2.5% S.R.A. Golden Yellow IX paste,
0.9% S.R.A. Heliotrope I paste,
0.45% C.R. Cotton Fast Brown R, and
10.0% Glauber's salt.

No. U-16: Black
- 0.4% S.R.A. Blue IV paste,
- 0.2% S.R.A. Golden Yellow III paste,
- 6.0% C.R. Cotton Fast Black B,
- 30.0% Glauber's salt,
- 1 gram per liter of olive oil soap, and
- 2 cubic centimeters per liter of Turkey-red oil.

### *Solid Black Shades*

In applying a solid black on acetate silk-cotton unions by means of dispersol dyes in combination with a direct cotton dyes,[2] such as Diazo Fast Black, the usual cross-dyeing procedure for the application of dispersol dyes should be reversed. In other words, the cotton should be dyed first with the direct dye, and then the acetate silk with the dispersol black (for instance, Celatene Black), in a separate bath. If the usual method of dyeing the acetate silk first is followed, the Celatene Black does not always go on well and the resulting shade may be brownish.

### *Two-Color Effects on Acetate Silk-Cotton Unions*

Two-color effects on acetate silk-cotton unions are obtained in the same manner and by the same processes as the solid color effects, except that more care must be exercised to avoid staining the accompanying fiber. For this reason it is sometimes advisable to use a two-bath process, dyeing the acetate silk with the dispersol dye first, and then dyeing the cotton in a separate bath. Another method, which corresponds more closely to this two-bath method and frequently gives even better results, is first to dye the acetate silk in a dispersol-dye bath and, when the exhaustion is practically complete, to start adding the direct dye, leaving the salt addition until near the last. In this process there is no danger of stripping some of the dispersol dye during the application of the direct dye, and when properly handled, excellent results are obtained. The following formulae are of interest for two-color effects on cotton or rayon-acetate silk unions.

*Formulae*

No. U-17: Celanese Flame, Cotton or Older Rayon Gray
- 2.0% S.R.A. Orange I paste,
- 0.5% S.R.A. Pure Yellow I paste,
- 0.3% C.R. Chlorazol Fast Gray or C.R. Cotton Fast Gray B, and
- 10.0% Sodium chloride or sulfate.

No. U-18: Celanese Deep Saxe, Cotton Gray
- 5.0% S.R.A. Blue II paste or 7.0% S.R.A. Blue IV paste,
- 0.3% C.R. Chlorazol Fast Gray or C.R. Cotton Fast Gray B, and
- 10.0% of sodium chloride or sulfate.

No. U-19: Celanese Crimson, Cotton Saxe
- 6.0% S.R.A. Red III paste,
- 1.2% S.R.A. Red V paste,
- 1.0% C.R. Chlorazol Fast Blue 2B or C.R. Cotton Blue 2B, and
- 20.0% of sodium chloride or sulfate.

No. U-20: Celanese Royal, Cotton Rose
- 7.5% S.R.A. Blue III paste or 8.0% S.R.A. Blue I paste,
- 0.25% C.R. Chlorazol Fast Red K or C.R. Cotton Fast Red BL, and
- 10.0% of sodium chloride or sulfate.

No. U-21: Celanese Cherry, Cotton Green
- 7.5% S.R.A. Red V paste,
- 2.0% C.R. Cotton Fast Blue 4GL }
- 0.7% C.R. Cotton Fast Yellow B } or 2.5% C.R. Chlorazol Fast Green, and
- 20.0% of sodium chloride or sulfate.

No. U-22: Celanese Violet, Cotton Green
- 5.0% S.R.A. Heliotrope I paste,
- 2.5% S.R.A. Fast Blue III paste,
- 2.5% C.R. Cotton Fast Green 2G or C.R. Chlorazol Fast Green, and
- 20.0% of sodium chloride or sulfate.

No. U-23: Celanese Brick, Cotton Gray
- 0.25% S.R.A. Orange I paste,
- 0.25% S.R.A. Red I paste,
- 0.3% C.R. Chlorazol Fast Gray or C.R. Cotton Fast Gray B, and
- 10.0% of sodium chloride or sulfate.

No. U-24: Celanese Lemon, Cotton Amethyst
2.5% S.R.A. Yellow III paste or 1.0% Pure Yellow I paste,
0.2% C.R. Chlorazol Fast Blue 2B or C.R. Cotton Blue 2B,
0.8% C.R. Chlorazol Violet R or C.R. Cotton Violet BBR, and
10.0 or 20% of sodium chloride or sulfate.

No. U-25: Celanese Bronze, Cotton Green
3.0% S.R.A. Golden Yellow VIII paste
0.5% S.R.A. Red I paste,
2.5% S.R.A. Blue III paste
or
3.0% S.R.A. Pure Yellow I paste,
0.5% S.R.A. Orange I paste,
2.5% S.R.A. Blue I paste, and

2.0% C.R. Cotton Fast Blue 4GL,
0.7% C.R. Cotton Yellow B,
or
2.5% C.R. Chlorazol Fast Green, and
20.0% of sodium chloride or sulfate.

No. U-26: Celanese Orchid, Cotton Sky Blue
1.0% S.R.A. Heliotrope I paste or Red V paste,
0.25% C.R. Chlorazol Sky Blue FF or C.R. Cotton Blue FF, and
10.0% of sodium chloride or sulfate.

No. U-27: Celanese Reseda, Cotton Brown
4.0% S.R.A. Golden Yellow VIII paste,
2.0% S.R.A. Blue IV paste,
or
4.0% S.R.A. Pure Yellow I paste,
1.5% S.R.A. Blue II paste;
2.5% C.R. Cotton Fast Brown R or C.R. Chlorazol Fast Brown No. 1, and
20.0% of sodium chloride or sulfate.

*Acetate Silk-Cotton or Rayon Hosiery or Knit Unions*

The dyeing of hosiery or other knit goods containing acetate silk in combination with cotton or the older rayons frequently presents a special problem, particularly where there are seams to be penetrated. In case of difficulty in penetrating these seams, a steeping operation is of great benefit in leveling, etc., especially in machine dyeing. It also aids in penetrating the cotton at the

restricted dyeing temperature of 80° C. (176° F.). The steep may be either cold or warm, either over-night or for a shorter period. Frequently the goods are simply allowed to remain in the scouring bath overnight, with excellent results.

In applying the S.R.A. dyes to Celanese-cotton hosiery, the Celanese manufacturers recommend that it be scoured by Method No. 6 and then allowed to remain in the scouring bath overnight. For the lighter shades, the union may be bleached as in Method No. 15 and antichlored as in Method No. 18. Small lots may be dyed by hand, but larger lots may be dyed either in a revolving drum or in the paddle machine. Copper or monel metal is advisable. The same general directions regarding the addition of dyestuff to the dye bath, etc., are followed as in dyeing other Celanese unions.

Dort[1] states that in dyeing Celanese-cotton hosiery, in order to insure proper penetration of the cotton tops, toes, and heels at a temperature of 82° C. (180° F.), direct cotton dyes should be selected which have the very best penetrating and leveling powers. These should be applied with as much as 10 cubic centimeters of Celascour per liter of dye bath. Where it is necessary to boil the cotton dyes onto the cotton, the method covered by British Patent No. 246,879[a] should be used. He recommends a 20 to 1 dye bath but states that satisfactory results have been obtained with a 10 to 1 bath. The following are examples of formulae which have given good results on Celanese-cotton or rayon unions:

*Formulae*

No. HU-1: Beige
- 0.7% S.R.A. Blue I paste,
- 0.5 S.R.A. Orange I paste,
- 0.9% S.R.A. Pure Yellow I paste,
- 0.125% C.R. Chlorazol Brown PB,
- 0.1% C.R. Chlorazol Orange AG,
- 0.01% C.R. Chlorazol Fast Orange R, and
- 10 % of salt.

Enter cold and dye at 75° C. (167° F.) for one and a half hours.

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[a] See Chapter XXV.

No. HU-2: Putty
1.25% S.R.A. Blue I paste,
0.1% S.R.A. Orange I paste,
1.0% S.R.A. Pure Yellow paste,
0.15% C.R. Chlorazol Drab RH,
0.025% C.R. Chlorazol Yellow G, and
10 % of salt.
Dye as in Formula No. HU-1.

No. HU-3: Light Gray
1.25% S.R.A. Blue I paste,
0.3% S.R.A. Orange I paste,
0.25% S.R.A. Pure Yellow paste,
0.1% C.R. Chlorazol Fast Gray, and
5% of salt.
Enter cold and dye at 65° C. (149° F.) for one and a half hours.

No. HU-4: Mole
6% S.R.A. Blue I paste,
1% S.R.A. Orange I paste,
2% S.R.A. Pure Yellow I paste,
0.5% C.R. Chlorazol Drab RH,
0.35% C.R. Chlorazol Brown RD, and
15% of salt.
Dye as in Formula No. HU-1.

No. HU-5: Flame
0.2% S.R.A. Blue I paste,
3.5% S.R.A. Orange I paste,
1.0% S.R.A. Red III paste,
1.2% Chlorazol Brown RK,
0.1% Chlorazol Brown M, and
10 % of salt.
Dye as in Formula No. HU-1.

No. HU-6: Tan
4% S.R.A. Blue I paste,
1.1% S.R.A. Orange I paste,
1.5% S.R.A. Pure Yellow I paste,
0.3% C.R. Chlorazol Drab RH,
0.25% Chlorazol Brown RK, and
10% of salt.
Dye as in Formula No. HU-1.

No. HU-7: Dark Brown
10% S.R.A. Blue I paste,
2% S.R.A. Orange I paste,
2% S.R.A. Pure Yellow I paste,
1.2% Chlorazol Brown RD,
0.15% Chlorazol Brown RK, and
20% of salt.
Dye as in Formula No. HU-1.

No. HU-8: Silver
0.3% S.R.A. Blue III paste,
0.08% S.R.A. Golden Yellow VIII paste, and
0.03% S.R.A. Heliotrope I paste,
0.1% Chloramine Fast Gray R, and
5.0% Glauber's salt.

No. HU-9: Maize
3.2% S.R.A. Golden Yellow IX paste,
0.12% S.R.A. Orange I paste,
1.5% C.R. Cotton Fast Yellow B,
0.16% C.R. Cotton Fast Orange 5R, and
0.04% C.R. Cotton Fast Blue FFB.

No. HU-10: Nude
0.075% S.R.A. Golden Yellow IX paste,
0.005% S.R.A. Orange I paste,
0.005% C.R. Cotton Fast Orange 5R,
0.005% C.R. Cotton Fast Scarlet 4BS, and
20.0% Glauber's salt.

No. HU-11: Stone
0.3% S.R.A. Blue III paste,
0.8% S.R.A. Golden Yellow IX paste,
0.2% S.R.A. Heliotrope I paste,
0.06% C.R. Cotton Fast Brown R,
0.01% C.R. Cotton Fast Gray B, and
5.0% Glauber's salt.

No. HU-12: Putty
0.4% S.R.A. Blue III paste,
0.5% S.R.A. Golden Yellow IX paste,
0.06% S.R.A. Heliotrope I paste,
0.015% C.R. Cotton Fast Gray B,
0.003% C.R. Cotton Fast Brown R,
0.001% C.R. Cotton Yellow B, and
5.0% Glauber's salt.

No. HU-13: Flesh
- 0.15% S.R.A. Orange I paste,
- 0.0072% C.R. Cotton Fast Brown R, and
- 0.0004% C.R. Cotton Fast Scarlet.

No. HU-14: Mushroom
- 0.3% S.R.A. Blue III paste,
- 0.1% S.R.A. Golden Yellow IX paste,
- 0.01 S.R.A. Red I paste,
- 0.01% C.R. Cotton Fast Gray B,
- 0.003% C.R. Cotton Fast Yellow B,
- 0.001% C.R. Chlorazol Fast Red BL, and
- 5.0% Glauber's salt.

No. HU-15: Cinnamon
- 0.6% S.R.A. Blue III paste,
- 6.0% S.R.A. Golden Yellow IX paste,
- 0.9% S.R.A. Heliotrope I paste,
- 0.45% C.R. Cotton Fast Brown R, and
- 10.0% Glauber's salt.

No. HU-16: Nigger
- 15.0% S.R.A. Blue III paste,
- 10.0% S.R.A. Golden Yellow VIII paste,
- 0.5% S.R.A. Red I paste,
- 4.0% C.R. Cotton Fast Brown R,
- 0.3% C.R. Cotton Fast Blue FFB, and
- 20.0% Glauber's salt.

No. HU-17: Navy
- 25.0% S.R.A. Blue III paste,
- 4.0% S.R.A. Golden Yellow IX paste,
- 4.0% S.R.A. Orange II paste,
- 2.5% C.R. Cotton Diazo Black BH, and
- 20.0% Glauber's salt.

*Black on Celanese-Cotton Hosiery and Knit Goods*

It is now recommended[3] to use Method No. 103 for a solid black on Celanese-cotton hosiery and knit goods. When the S.R.A. Fast Black Developer HY Special is used it is no more difficult to obtain a fast black on these mixed goods than to obtain a developed black upon cotton alone. The only difference between this process and that generally used for cotton is that the acidified developing bath is used warm, instead of cold.

*Method No. 103: Developed Black on 50-50 Celanese and Cotton Knit Goods.* Enter the goods into a 20 to 1 dye bath at 45° C. (113° F.) containing 10 per cent of S.R.A. Black IV and 4 to 6 per cent of Chlorazol Black LF or Diamine Fast Black C conc. Raise the temperature during an hour or an hour and a half to 75° C. (167° F.), adding 40 per cent of sodium chloride in portions. Rinse the goods before diazotizing.

*Method No. 103-A: Diazotizing Black on Knit Goods.* Diazotize the goods in a 20 to 1 bath for one hour with 5 per cent of 98 per cent sodium nitrite and 14 per cent of 28 per cent hydrochloric acid.

*Method No. 103-B: Developing Black on Knit Goods.* Dissolve 1 to 1.5 per cent of sodium hydroxide, on the weight of the fiber, in water and work 2 or 3 per cent of S.R.A. Black Developer HY Special into a paste with it, adding hot water to complete the solution. Dissolve 5 per cent of glue, also on the weight of the goods, in water and add it to the 25 to 1 developing bath; then add the dissolved developer to the bath. Lastly add 5 per cent of 80 per cent formic acid to the bath and stir well. Enter the goods and raise the temperature to 60° C. (140° F.) during an hour. When the development is complete, rinse in water at about 45° C. (113° F.), then in cold water, and finally soap well in a bath containing 0.5 to 1 gram per liter of olive oil soap. Then rinse well again.

### *The Celatene Dyes on Acetate Silk-Cotton Unions*

The Celatene dyes resemble the S.R.A. dyes in many ways and are applied by the same general methods to acetate silk-cotton unions. While most direct dyes may be applied to cotton in the same dye bath and concurrently with the application of the Celatene dyes to the acetate silk, in order to obtain colors of similar fastness on both fibers, it is desirable to use vat dyes on the cotton, as described in Chapter XXIX. This of course necessitates the use of the two dye baths. The Caledon vat dyes have proven particularly useful for this purpose, but many of the vat dyes mentioned in the list for vat dyes on Celanese-cotton unions may also be used in the same way. Some Celatenes stain cotton slightly, but it may be cleared by the methods given under Clearing Unions, Chapter XXXV.

The Duranol and Dispersol dyes have no affinity for cotton, the older rayons or other vegetable fibers and may therefore be used on acetate silk-cotton unions to excellent advantage by the usual methods, such as those given in Chapter XXII, with the precautions mentioned in the foregoing paragraphs.

The Direct Azonines do not appreciably stain cotton and may readily be used to obtain two-color effects on acetate silk-cotton unions. As usual in dyeing such unions, the acetate silk should be dyed first and then the cotton dyed at not over 40 to 60° C. (105 to 120° F.) with the addition of Glauber's salt, but without the addition of sodium carbonate, using such dyes as do not stain the acetate silk.

The "Extra Pastes for Acetate Silk" of the Badische Company are also applicable to acetate silk-cotton unions. When applied in light shades, the cotton usually remains unstained, but heavier dyeings generally tint the cotton somewhat. They may be applied in the same dye bath with most of the direct cotton dyes. For two-colored effects upon acetate silk-cotton unions by the single bath method, 5 to 20 per cent of calcined Glauber's salt should be added to the dye bath as given in Method No. 81. All soda or other alkalines should be strictly avoided. Solid shades are dyed in the same manner. Care should be taken that both fibers are alike in tone, but the acetate silk rather on the light side of the cotton.

The Celanthrene dyes can be used upon cotton-acetate silk unions for either cotton-white or two-colored effects. Their fastness to light suggests the use of vat dyestuffs upon the accompanying cotton, as mentioned in Chapter XXIX. Where cotton-white effects are desired, the Celanthrenes are applied as in Chapter XXII. In some cases it may be necessary to clear the cotton by means of a light soaping, as in Method No. 112.

### *References*

[1] R. G. Dort, *American Dyestuff Reporter 15*, 258-66 (1926).
[2] W. M. Todd, *Dyer and Calico Printer 55*, 126 (1926).
[3] American Cellulose and Chemical Co., "Practical Notes on Dyeing Celanese." Celanese Dyeing Leaflet No. 2, 3rd Edition.
[4] R. G. Dort, *Chemicals 25*, No. 1, 22-6 (1926).

# CHAPTER XXXIII

## DIRECT COTTON DYES WHICH LEAVE ACETATE SILK WHITE

In any discussion of the dyeing of combinations of acetate silk with other fibers, the study of the direct cotton dyes which leave acetate silk either white or only very slightly stained is of the utmost importance. Whether the acetate silk is to be present as white, or with undyed effects, dyed in a contrasting, or even in a similar shade, much better results are obtained by using dyestuffs for each fiber which give a minimum of staining on the accompanying fibers, due to the better control of the resulting shades. However, it is of course obvious that the direct cotton dyes which stain or dye acetate silk may have a certain field of usefulness for solid color effects on acetate silk-cotton or rayon unions, but usually much better and brighter shades are obtained on the acetate silk, by the use of the special dyes for this fiber.

Certain direct browns, reds, and greens have a particular inclination to stain acetate silk slightly, and in applying these products, or in fact in dyeing any unions of two or more fibers where it is desired to leave one fiber white, it is always best to add the dye to the bath in small quantities at the start, and only add more dye to the bath as the liquor is exhausted by the fiber to be dyed. In the case of direct cotton dyes, the salt should be added only after the bath has been brought up to temperature. In this way the fiber to be dyed, which naturally should have the greatest affinity of the two fibers for the dyes used, is dyed with a minimum of dyestuff and no excess of dye should be allowed in the bath. The presence of dyeing assistants and leveling agents, as well as the use of a long dye bath, all assist in keeping the one fiber white. Sodium chloride is frequently preferable, in place of the sulfate, to aid exhaustion. Method No. 105 has been recommended for white acetate silk effects.

*Method No. 105: White Acetate Silk Effects in Acetate Silk-Colored Cotton Unions.* The direct cotton dye should be applied in

a 20, or better yet, 30 to 1 dye bath, containing the necessary amount of dyestuff and 20 to 30 per cent of sodium chloride or sulfate. The thoroughly wet-out goods are entered and worked for an hour at 71 to 76° C. (160 to 170° F.). For blacks it is advisable to raise the temperature to 80 to 85° C. (175 to 185° F.) and use about 40 per cent of salt to insure penetration. Alkaline baths should be avoided, and the dyed goods should be rinsed well and soaped to clear the acetate silk. This is followed by another thorough rinsing. Turkey-red oil will aid penetration and leveling, and is therefore especially useful for light shades.

From our study of the chemical composition and properties of the different brands of acetate silk, it is obvious that the staining properties of the various direct cotton, as well as any other class of dyestuffs, may vary somewhat on the different products. While most of the information concerning the staining properties of the various dyes on acetate silk is rather general, it may be assumed that in most instances it has particular reference to Celanese. The Newport Chemical Works has made a more detailed study of the matter in connection with their products, and the following is a summary of their results. As a rule it may be assumed that the staining properties of Rhodiaseta, and the other brands of acetate silk more closely approximate those of Celanese than Lustron.

Direct cotton dyes leaving Celanese white:

*Yellow*

Newport Chrysophenine Extra
Newport Direct Yellow G
Newport Direct Fast Yellow NN
Newport Direct Pure Yellow S

*Orange*

Newport Direct Orange 2RG and 2R
Newport Direct Fast Orange RS

*Blue*

Newport Direct Sky Blue, and the FF brand
Newport Direct Fast Blue 4GL, SFF, and SFR
Newport Benzo Azurine G Extra
Newport Direct Blue BH Extra conc., 2B conc., BX, 3BX, and RS
Newport Direct Brilliant Blue G

*Red*

Newport Direct Fast Scarlet G, 4BA, and 8BA
Newport Direct Fast Red 8BL, and F
Newport Benzo Purpurine 4B conc., and 10B conc.
Newport Direct Garnet R

*Pink*

Newport Direct Pink 12B Special, and EBN
Newport Direct Pink 2B

*Brown*

Newport Direct Brown CR, GRN, and N3G
Newport Direct Fast Brown M, BT, and T2G
Newport Union Brown No. 17881

Direct cotton dyes leaving Lustron white:

*Black*

Newport Direct Fast Black WCT

*Violet*

Newport Direct Violet N

*Gray*

Newport Neutral Gray GG

*Yellow*

Newport Direct Pure Yellow S
Newport Chrysophenine Extra
Newport Direct Fast Yellow NN
Newport Direct Yellow G

*Orange*

Newport Direct Orange 2RG, and R
Newport Direct Fast Orange RS

*Blue*

Newport Direct Blue BH Ex conc., 2B conc., 3BX, and RS
Newport Direct Fast Blue SFF, 2GL, 4GL, FF, and SFR
Newport Direct Sky Blue

*Red*

Newport Direct Fast Scarlet G, 4BA, 4BS, and 8BA
Newport Benzo Purpurine 4B conc., and 10B conc.
Newport Direct Garnet R
Newport Direct Fast Red F

*Pink*

Newport Direct Pink 2B
Newport Direct Fast Pink E2GN, 12B special, and EB Extra

*Brown*

Newport Direct Fast Brown BT
Newport Direct Bown XR

*Violet*

Newport Direct Violet N

Direct Cotton Dyes Which Leave Lustron Effects Slightly Stained:

*Orange*

Newport Direct Orange 2R

*Brown*

Newport Direct Brown GXR
Newport Direct Brown RXN

Direct Cotton Dyes Which Leave Lustron Effects Badly Stained:

*Black*

Newport Direct Black EG Extra

*Brown*

Newport Direct Brown RG
Newport Direct Fast Brown M

*Blue*

Newport Direct Fast Blue RW

*Violet*

Newport Direct Brilliant Violet R conc.

Cotton Dyes Leaving Rhodiaseta white:

Naphthamine Yellow BN and GN
Chrysophenine GK
Naphthamine Orange 2R (C.I. No. 621)
Naphthamine Fast Scarlet E4B and E8B
Naphthamine Fast Red R
Cotton Fast Violet B
Naphthamine Blue 2B and 12B
Naphthamine Black CE and WR
Naphthamine Fast Green G
Naphthamine Brown H and T
Naphthamine Fast Gray B
Diazogene Black 53861 developed with resorcinol

The American Cellulose and Chemical Company gives the following list of direct cotton dyes which leave Celanese white and which have good fastness to light and washing:

*Black and Grays*

Chloramine Fast Gray R (Sandoz)
C.R. Cotton Black B (Celanese)
C.R. Cotton Black FWW (Celanese)
Direct Black A-68396 (National)

*Blue*

Chlorantine Fast Blue 8GL (Ciba)
Chlorantine Fast Blue GLM (Ciba)
Chlorantine Fast Blue RL (Ciba)
C.R. Cotton Fast Blue FFB (Celanese)
C.R. Dianol Fast Blue 2BM (BDC and DCA)
Pontamine Fast Blue 2GL (Du Pont)
Pontamine Fast Blue 4GL (Du Pont)
Solantine Blue 4GL (National)
Solantine Blue RL (National)

*Brown*

C.R. Cotton Fast Brown R (Celanese)
Erie Fast Brown 2RB (National)

*Green*

Chlorantine Fast Green BL (Ciba)

*Orange*

Pontamine Fast Orange EG (Du Pont)
Solantine Orange A (National)

*Red and Pink*

Chlorantine Fast Bordeaux BL (Ciba)
Chlorantine Fast Rubine RL (Ciba)
C.R. Cotton Fast Red BL (Celanese)
Direct Fast Ereca 2BW (Ciba)
Solantine Red 8BLM (National)

*Violet*

Direct Fast Heliotrope BL (National)
Solantine Violet R (National)

*Yellow*

C.R. Cotton Fast Yellow B (Celanese)
Erie Fast Yellow WB (National)
Fast Yellow NN (Newport)
Pontamine Fast Yellow NN (Du Pont)
Pontamine Yellow CH (Du Pont)

The same authority also gives the following list of direct cotton dyes which leave Celanese white and which have good fastness to light (those marked L) or washing (W) but not always to both:

*Black and Gray*

C.R. Cotton Diazo Black BH (L) (Celanese)
Diazine Black BO (L) (National)
Diazo Black BH extra conc. (L) (Newport)
Pontamine Fast Gray B (L) (Du Pont)

*Blue*

Chloramine Fast Blue BS (L) (Sandoz)
Direct Fast Blue SFR (L) (Newport)
Niagara Blue 3B (W) (National)
Niagara Blue NR (W) (National)
Pontamine Navy Blue DB (W) (Du Pont)

*Brown*

C.R. Chlorazol Fast Brown RD (W) (BDC & DCA)
Direct Fast Brown BT (W) (Newport)
Erie Brown CN (W) (National)

*Orange*

Chloramine Fast Orange SE (L) (Sandoz)
C.R. Dianol Fast Orange 2G (W) (BDC & DCA)
Direct Orange 2R (W) (Newport)

*Red and Pink*

C.R. Cotton Fast Pink 2B (L) (Celanese)
C.R. Cotton Fast Scarlet 4BS (W) (Celanese)
C.R. Dianol Fast Red K (L) (BDC & DCA)
C.R. Dianol Scarlet 4BS (W) (BDC & DCA)
Direct Fast Pink 2B (W) (Newport)
Direct Fast Red 8BL (L) (Newport)
Direct Fast Scarlet G (L) (Newport)
Direct Fast Scarlet 4BA (W) (Newport)
Direct Fast Scarlet 8BA (W) (Newport)
Erie Scarlet 8BA (W) (National)
Pontamine Fast Pink G (W) (Du Pont)
Pontamine Fast Scarlet 4BS (L) (Du Pont)

*Violet*

Chloramine Fast Violet B (L) (Sandoz)
Chlorantine Fast Violet 4BL (L) (Ciba)
C.R. Cotton Fast Violet BL (L) (Celanese)

*Yellow*

C.R. Cotton Fast Yellow A (W) (Celanese)
Erie Yellow 2RF (W) (National)
Erie Yellow Y (L) (National)
Pontamine Yellow GR (W) (Du Pont)
Pontamine Yellow SXG (W) (Du Pont)
Pontamine Yellow SXR (W) (Du Pont)
Solantine Yellow A (W) (National)
C.R. Dianol Fast Yellow AD (W) (BDC & DCA)

From the same source, direct cotton dyes which leave Celanese white and have fair fastness to light and washing:

*Black and Gray*

Chlorantine Fast Gray BLN (Ciba)
Chlorantine Fast Gray GLN (Ciba)
Chloramine Fast Gray B (Sandoz)
C.R. Cotton Black 3G (Celanese)
Diazine Black RS (Newport)
Pontamine Fast Black CW (Du Pont)
Diazo Black HEX (National)

*Blue*

Chlorantine Fast Blue 2GL (Ciba)
C.R. Cotton Blue FF (Celanese)
C.R. Cotton Blue 2B (Celanese)
C.R. Cotton Fast Blue 4GL (Celanese)
C.R. Cotton Sky Blue (Celanese)
C.R. Dianol Fast Blue 4GL (BDC & DCA)
C.R. Dianol Sky Blue 5BX (BDC & DCA)
Diazo Fast Blue 6GW (Ciba)
Direct Fast Blue SFF (Newport)
Direct Sky Blue FF (Newport)
Fast Blue 4GL (Newport)
Niagara Blue DB (National)
Niagara Blue 2B (National)
Niagara Blue HW (National)
Niagara Sky Blue (National)
Niagara Sky Blue 6B (National)
Pontamine Blue BBF (Du Pont)
Pontamine Blue CLG (Du Pont)
Pontamine Blue GH conc. (Du Pont)
Pontamine Fast Blue SLN (Du Pont)
Pontamine Sky Blue 5BX (Du Pont)

*Brown*

C.R. Chlorazol Brown B Extra (BDC & DCA)
C.R. Chlorazol Fast Brown B Extra (BDC & DCA)
C.R. Chlorazol Fast Brown RK (BDC & DCA)
Erie Catechine 3G (National)

*Green*

C.R. Cotton Green 2G (Celanese)

*Orange*

Chlorantine Fast Orange 2RL (Ciba)
C.R. Cotton Fast Orange 5R (Celanese)
Erie Fast Orange A (National)
Erie Fast Orange CG (National)
Pontamine Fast Orange S (Du Pont)
Pontamine Orange 4G (Du Pont)
Pontamine Orange R (Du Pont)

*Red and Pink*

Chlorantine Fast Bordeaux 2BL (Ciba)
Chlorantine Fast Red 7BL (Ciba)
Erie Fast Scarlet 4BA (National)
Erie Fast. Scarlet YA (National)
Erie Pink 2B (National)
Pontamine Fast Red SBL (Du Pont)
Pontamine Fast Scarlet 8BS (Du Pont)

*Violet*

C.R. Cotton Violet BBR (BDC & DCA)

*Yellow*

Chrysophenine Extra (National)
C.R. Dianol Fast Yellow BS (BDC & DCA)
Direct Yellow G (Newport)
Erie Yellow F (National)
Pontamine Yellow SX (Du Pont)

The following direct cotton dyes from various sources have been stated to leave the accompanying acetate silk white. Undoubtedly they will vary widely in this property as in all others, but most of them will give good results when used for light shades by the proper methods:

*Yellow*

Oxydianil Yellow G and O (MLB)
Dianil Direct Yellow S (MLB)
Direct Golden Yellow 2G (Ciba)
Direct Yellow TG Extra conc., and TR conc. (Ciba)
Dianil Yellow GC, and 2R (MLB)
C.R. Chlorazol Yellow G (BDC)
C.R. Chlorazol Fast Yellow B, FG, and NX (BDC)
Direct Fast Yellow 3G conc. (Ciba)
Paramine Fast Yellow 3G (Holliday)
Chrysophenine G (Union Dye)
Diamine Yellow CP (Cassella)
Oxy Diamine Yellow GG and TZ (Cassella)
Oxyphenine GGX (Ciba)
Stilbene Yellow GX, and 3GX (Badische)
Diamine Fast Yellow A, B, 4G, FF, M, and R (Cassella)
C.R. Cotton Yellow 3G (Celanese)
C.R. Chlorazol Cotton Fast Yellow B (BDC)
Stilbene Yellow G and 3G (Badische)
Benzo Fast Yellow RL (Bayer)
Diamine Fast Yellow B, G, and 4G (Cassella)
Art Silk Bright Yellow CW (Geigy)
Art Silk Chrysoine RCW (Geigy)
Chloramine Fast Yellow B (Bayer)
Chloramine Yellow M (Bayer)
Direct Yellow R Extra (Bayer)
Pontamine Diazo Yellow 2GL (Du Pont)
Pontamine Fast Yellow B (Du Pont)

*Orange*

Dianil Fast Orange 2R and O (MLB)
Direct Brilliant Orange RAF Extra conc. (Ciba)
Direct Fast Orange SE (Ciba)
C. R. Chlorazol Cotton Fast Orange 5R (BDC)
Paramine Fast Orange D, and G (Holliday)
Pyramine Brilliant Orange 3RS (Holliday)
Chlorazol Fast Orange AG (BDC)
Pontamine Fast Orange 2G and ER (Du Pont)
Art Silk Orange BCW (Geigy)
Art Silk Fast Orange RCW (Geigy)
Dianil Orange G (MLB)
Direct Brilliant Orange RAF Extra conc. (Ciba)
Diamine Brilliant Orange SS (Cassella)
Diamine Fast Orange EG and ER (Cassella)
Diamine Orange D and G (Cassella)
Benzo Fast Orange WS (Bayer)
Chloramine Orange G (Bayer)
C.R. Chlorazol Fast Orange R and AG (BDC and DCA)

*Red and Pink*

Diamine Fast Red 8BL (Cassella)
Diamine Brilliant Rubine S (Cassella)
Diamine Azo Scarlet 4BL Extra, 6BL Extra, 8BL Extra. Diazotized and developed with *B*-naphthol (Cassella)
Diamine Azo Fast Red 5B, 6B. Diazotized and developed with *B*-naphthol (Cassella)
Diamine Azo Bordeaux B, R. Diazotized and developed with *B*-napththol (Cassella)
Dianil Light Red 6BL, and 8BW (MLB)
Dianil Fast Red K (MLB)
Thiazine Red GXX (Badische)
Direct Fast Scarlet BCW, 3BCW and SCW (Noil)
Direct Fast Red FCW (Noil)
Pontamine Fast Pink BL (Du Pont)
Pontamine Fast Scarlet 4BS (Du Pont)
Pontamine Red 12B Conc. (Du Pont)
Pontamine Diazo Red 5BL and 7BL (Du Pont)
Pontamine Diazo Bordeaux 7BL (Du Pont)
Oxyamine Fast Pink B (Badische)
Thiazine Red G and R (Badische)
Cotton Pink GN and BN (Badische)
Benzo Fast Eosine BL (Bayer)
Benzo Fast Pink 2BL (Bayer)
Benzo Fast Red 8BL (Bayer)
Art Silk Fast Red CW (Geigy)
Art Silk Red FCW (Geigy)
Dianil Light Red 8BW, and 12BW (MLB)
Direct Rose T
Cotton Red A
Oxamine Light Pink BBX (Badische)
Pontamine Diazo Scarlet 2BW (Du Pont)
Direct Garnet BCW (Noil)
Paramine Fast Pink B (Holliday)
C.R. Chlorazol Fast Pink BK (BDC)
C.R. Chlorazol Fast Red K (BDC)
C.R. Chlorazol Scarlet 4BS (BDC)
C.R. Chlorazol Fast Eosine B (BDC)
C.R. Chlorazol Fast Bordeaux LK (BDC)
C.R. Chlorazol Cotton Fast Red BL (BDC)
Chlorantine Fast Red 5BL (Ciba)
Diamine Fast Bordeaux 6BS (Cassella)
Diamine Brilliant Bordeaux R (Cassella)
Dianil Fast Scarlet 4BSN, 5BSN, and 7BSN (MLB)
Dianil Pink BD (MLB)
C.R. Chlorazol Cotton Fast Pink 2B (BDC)
Diamine Fast Rose B, BBF, and G (Cassella)
Diamine Rose B Extra, BD, FFB, FFB Extra, and GD (Cassella)
Diamine Brilliant Scarlet S (Cassella)
Diamine Fast Scarlet 7BS, 8BS, and GFF (Cassella)

*Violet*

C.R. Chlorazol Cotton Fast Violet BL (BDC)
C.R. Chlorazol Violet R (BDC)
Diamine Heliotrope B (Cassella)
Diamine Fast Violet FFBN, and FERN (Cassella)
Diamine Fast Red Violet FR (Cassella)
Direct Violet NCW (Noil)
Pontamine Diazo Violet BL (Du Pont)
Chloramine Violet FFB (Bayer)
Chlorantine Fast Violet 4BLN, and 2RL (Ciba)
Pontamine Brilliant Violet (Du Pont)

*Blue*

Melanthrine BHX (Ciba)
Chlorantine Fast Blue 4GL (Ciba)
C.R. Chlorazol Blue B, and 3B (BDC)
C.R. Chlorazol Sky Blue FF, and GW (BDC)
C.R. Chlorazol Fast Blue 2B and 2BN (BDC)
C.R. Chlorazol Cotton Fast Blue 4GL, and FFB (BDC)
Direct Blue A
Direct Deep Blue CW (Noil)
Dianil Pure Blue PH (MLB)
Dianil Fast Blue RL, GL, and 4GL (MLB)
Paramine Sky Blue FF (Holliday)
Paramine Blue 2B New (Holliday)
Diamineral Blue BF (Casella)
Diaminogene Blue NBB. Diazotized and developed with *B*-naphthol (Cassella)
Diaminogene Sky Blue. Diazotized and developed with *B*-naphthol (Cassella)
Dianil Blue H6G (MLB)
Brilliant Dianil Blue 3G
Direct Blue 2B Conc., and 3B conc. (Ciba)
Diamine Fast Blue F3B, F3G, FFB, and FFG (Cassella)
Diamine Blue 3B (Cassella)
Diamine Brilliant Blue G (Cassella)
Diamine Fast Brilliant Blue R Cassella)
Diamine Sky Blue FF (Cassella)
Diamine Dark Blue B (Cassella)
Oxy Diamine Blue PG (Cassella)
Dianil Blue H3G, H2G, B, G, and R (MLB)
Direct Navy RCW (Noil)
Diaminogene B, diazotized and developed with resorcinol or *B*-naphthol (Cassella)
Oxamine Blue B, 3B, 4B, 5B, and GN (Badische)
Oxamine Light Blue B, BG, and G (Badische)
Oxamine Pure Blue 5B, and 6B (Badische)
Direct Blue 2BCW (Noil)
Cotton Brilliant Blue RCW (Noil)
C.R. Cotton Diazo Blue BH (Celanese)
C.R. Cotton Fast Blue 4GL (Celanese)
Pontamine Fast Blue RL (Du Pont)
Pontamine Sky Blue 6BX (Du Pont)
Pontamine Diazo Blue BR, and 3G (Du Pont)
Oxamine Dark Blue BG (Badische)
Art Silk Fast Blue CW (Geigy)
Art Silk Bright Blue CW (Geigy)
Benzo Fast Blue 4GL and FFL (Bayer)
Benzo Sky Blue (Bayer)
Brilliant Fast Blue 3BX (Bayer)
Direct Sky Blue A conc., and 6B conc. (Ciba)

*Green*

Erie Green MRS (National)
Direct Green BCW (Noil)
Direct Dark Green BGCW (Noil)
Erie Blue Green CW (National)
C.R. Chlorazol Fast Green (BDC)
Chlorantine Fast Green B (Ciba)
Diamine Nitrazole Green BB coupled with Nitrazole CF (Cassella)
Diamine Green HS (Cassella)
Diamine Dark Green NZ (Cassella)

*Brown*

Erie Brown 3RB (National)
Direct Brown CCW, RCW, MCW and BCW (Noil)
Direct Fast Brown AHPCW (Noil)
C.R. Cotton Drab Brown L (Celanese)
C.R. Cotton Brown 2RL (Celanese)

Chlorantine Fast Brown 3GL (Ciba)
C.R. Cotton Tan CH
C.R. Chlorazol Drab RH (BDC)
C.R. Chlorazol Brown PB (BDC)
C.R. Chlorazol Nigger Brown (BDC)
C.R. Chlorazol Fast Brown No. 1, and No. 2 (BDC)
C.R. Chlorazol Cotton Brown 2RL (BDC)
C.R. Chlorazol Cotton Drab Brown L (BDC)
Diamine Bronze Brown PE (Cassella)
Diamine Fast Brown GB (Cassella)
Pontamine Fast Brown RK (Du Pont)
Art Silk Tan CW (Geigy)
Art Silk Nigger Brown CW (Geigy)

*Black and Gray*

Benzo Fast Black L (Bayer)
Erie Black NR (National)
Dianil Black A2B, ES, and FDX (MLB)
Paramine Black BH, and SW (Holliday)
Paramine Burl Black RMW (Holliday)
Direct Black GS
Zambesi Black V (AGAF)
Diamine Black HW (Cassella)
Diamine Black BH diazotized and developed with resorcinol or *B*-naphthol (Cassella)
Diaminogene OB and OT diazotized and developed with resorcinol or *B*-naphthol (Cassella)
Oxamine Black BHN (Badische)
Noppen Black B
Cotton Black 3GCW (Noil)
Develop Black BHCW (Noil)
C.R. Chlorazol Black BH and GF (BDC)
Direct Fast Black HWCW (Noil)
C.R. Cotton Fast Black 3G (Celanese)
Chlorazol Black LF (BDC)
Diamine Fast Black C conc. (Cassella)
Plutamine Black A
C.R. Cotton Black M (Celanese)
Dianol Black DL (MLB)
Diazo Black BHN (Bayer)
Direct Black VT (Bayer)
Pontamine Diazo Black BH conc. (Du Pont)
Pontamine Fast Black LN (Du Pont)
Diazo Black RS (Newport)
Oxamine Black RN and BHN, diazotized and developed with resorcinol (Badische)
Oxydiamine Black JW Extra conc. (Cassella)
Art Silk Jet Black CW (Geigy)
Art Silk Black CW (Geigy)
Oxamine Light Gray EB (Badische)
Dianil Fast Gray 2BN, and 2BL (MLB)
C.R. Chlorazol Drab RH (BDC)
C.R. Chlorazol Fast Gray (BDC)
Diamine Fast Gray BN (Cassella)
Diamine Gray G (Cassella)
C.R. Cotton Fast Gray B (Celanese)
C.R. Chlorazol Fast Black N (BDC and DCA)
C.R. Chlorazol Black and LH (BDC and DCA)
Cotton Black AC (Badische)

Certain direct cotton dyes withstand diazotization and development very well and for this reason are particularly adapted for certain work where the developed colors are to be used on the acetate silk. The following dyes belong to this class and do not stain Celanese:

C.R. Chlorazol Fast Scarlet 4BS
C.R. Chlorazol Fast Orange AG and R
C.R. Chlorazol Fast Yellow B, FG and NX
C.R. Chlorazol Fast Blue 2BN
C.R. Chlorazol Yellow GX
C.R. Chlorazol Green
C.R. Chlorazol Dark Green PL

Direct cotton dyes which stain Celanese very slightly by Method No. 105:

Du Pont Thioflavine S
Pontamine Fast Yellow 4GL
Pontamine Light Yellow 5GX
Pontamine Brown R
Du Pont Purpurine 4B conc., and 10B conc.
Pontamine Bordeaux B
Pontamine Scarlet B
Pontamine Violet N
Pontamine Blue AX
Pontamine Copper Blue RRX
Pontamine Brilliant Green GX
Pontamine Diazo Orange
Pontamine Diazo Scarlet A, and R

The following Ciba direct cotton dyes stain Celanese slightly:

Chlorantine Fast Yellow RL and 4GL
Direct Fast Scarlet SE
Direct Rubine Conc.
Chlorantine Fast Violet BL
Cupranil Brown G (A union dye)
Direct Brown M Conc., and MR Conc.
Chlorantine Fast Black BL

The following direct cotton dyes stain acetate silk more or less, particularly in a short dye bath or in the application of heavy shades and are therefore not recommended for acetate silk white or contrasting color effects:

*Yellow*

Aurophenine O (MLB)
Pyramine Yellow G (Badische)
Dianil Yellow 3G (MLB)
Oxamine Fast Yellow B (Badische)

*Orange*

Cotton Orange G and R (Badische)
Pyramine Brilliant Orange 3RS
Dianil Orange GS (MLB)

*Red and Pink*

Cotton Fast Red 8BS (Badische)
Oxamine Light Red 4B and E8B (Badische)
Oxamine Light Pink BX (Badische)
Dianil Fast Scarlet 8BS, and GSN (MLB)
Dianil Light Red 8BL, and 12BL (MLB)
Cotton Pink BN, and GN (Badische)
Thiazine Red R (Badische)
Dianil Pink BD (MLB)
Oxamine Brilliant Red B (Badische)

*Violet*

Oxamine Violet (Badische)
Oxamine Brilliant Violet B, and RR (Badische)
Oxamine Light Violet B, and RR (Badische)
Direct Fast Violet 4B (Peerless)

*Blue*

Oxamine Dark Blue BG (Badische)
Dianil Fast Blue RL (MLB)
Brilliant Dianil Blue 6G, and R (MLB)

*Brown*

Thiazine Brown G and R (Badische)

*Black*

Burl Black B (Badische)
Chlorazol Black E Extra (stains Celanese a deep reddish-gold)
Cotton Black AC (Badische)
Oxamine Black RN (Badische)

The following direct cotton dyes are sometimes used to dye acetate silk and may therefore have a certain usefulness on acetate silk-cotton unions for solid shades:

Paramine Orange G and R
Pyramidol Brown BG
Paramine Yellow 2G
Paramine Brown G

The following cotton and union dyes have been suggested as suitable for use on unions containing acetate silk white or contrasting colored effects:

Diamine Fast Yellow A, B, FF, M, and R (Cassella)
Oxydiamine Yellow TZ (Cassella)
Diamine Yellow CP (Cassella)
Union Fast Yellow G (Cassella)
Diamine Orange D (Cassella)
Diamine Brilliant Orange SS (Cassella)
Diamine Fast Scarlet 4BS, and 7BS (Cassella)
Diamine Rose BD, and GD (Cassella)
Diamine Fast Rose BBF (Cassella)
Diamine Fast Red 8BL (Cassella)
Diamine Fast Rubine FB (Cassella)
Diamine Brilliant Bordeaux R (Cassella)
Diamine Fast Red Violet FR (Cassella)
Diamine Heliotrope B (Cassella)
Diamine Fast Brown GF (Cassella)
Diamine Fast Blue C, CG, F3B, FFG, and F3G (Cassella)
Oxydiamine Blue 5G, PB, and PG (Cassella)
Diamine Fast Brilliant Blue R (Cassella)
Diamineral Blue R (Cassella)
Diamine Steel Blue L (Cassella)
Diamine Brilliant Blue G (Cassella)
Diamine Dark Blue B (Cassella)
Union Fast Blue MB, and FR (Cassella)
Union Fast Gray BR (Cassella)
Oxydiaminogene OB (Cassella)
Diamine Black BH (Cassella)
Para Diamine Black BF Extra conc., and FFB Extra conc. (Cassella)
Union Black VA
Diamine Azo Scarlet 4BL Extra 6BL Extra, and 8B Extra diazotized and developed with *B*-naphthol (Cassella)
Diamine Azo Fast Red 5B, and 6B diazotized and developed with *B*-naphthol (Cassella)
Diamine Azo Bordeaux B, R, and K3B diazotized and developed with *B*-naphthol (Cassella)
Diamine Azo Navy Blue B conc. diazotized and developed with *B*-naphthol (Cassella)
Diaminogene Blue GG and NBB diazotized and developed with *B*-naphthol (Cassella)

The following cotton and union dyes stain acetate silk more or less and therefore should not be used for heavy shades on wool in the presence of acetate silk white or contrasting colored effects:

Diamine Fast Yellow 4G (Cassella)
Diamine Fast Orange ER (Cassella)
Diamine Scarlet 10BS, and GG (Cassella)
Diamine Purpurine 6B (Cassella)
Diamine Heliotrope G (Cassella)
Union Fast Heliotrope B (Cassella)
Diamine Red 4B (Cassella)
Diamine Brilliant Rubine S (Cassella)
Diamine Violet Red (Cassella)

Diamine Violet N (Cassella)
Diamine Fast Violet BBN and FFBN (Cassella)
Oxydiamine Violet B (Cassella)
Union Violet KB (MLB)
Chlorazol Fast Heliotrope BK
Diamine Brown ATC, and M (Cassella)
Diamine Fast Brown GB, and R (Cassella)
Diamine Catechine 3G (Cassella)
Union Fast Brown G (Cassella)
Diamine Green G (Cassella)
Union Fast Green GG (Cassella)
Diamineral Blue BB. and CVB (Cassella)
Diamineral Brilliant Blue B (Cassella)
Union Sky Blue KF (Cassella)
Union Blue BB, BJ, KG, and KHS (Cassella)
Union Navy Blue KPB, and KO (Cassella)
Union Gray BBG (Cassella)
Diaminogene Extra, and B (Cassella)
Diamine Black HW (Cassella)
Oxydiamine Black A (Cassella)

The following cotton and union dyes stain aceate silk considerably and are therefore not suited for acetate silk white or contrasting color effects. Some may prove useful for solid shades:

Thioflavine S (Cassella)
Diamine Orange B and F Cassella)
Oxydiamine Orange G (Cassella)
Union Fast Orange G and R (Cassella)
Diamine Scarlet B and 3B (Cassella)
Diamine Fast Red F (Cassella)
Diamine Red 6B, and 10B (Cassella)
Union Fast Red R (Cassella)
Diamine Purpurine B (Cassella)
Diamine Bordeaux B, and S Cassella)
Diamine Fast Bordeaux 6BS (Cassella)
Union Fast Bordeaux FR (Cassella)
Diamine Brown MR, and B (Cassella)
Oxydiamine Brown 3GN, G and RN (Cassella)
Diamineral Brown G (Cassella)
Diamineral Catechine G, and B (Cassella)
Union Fast Brown GG, L, TD, and MP (Cassella)
Union Dark Brown A (Cassella)
Oxydiamine Violet G, and BF (Cassella)
Diamine Green B, and HS (Cassella)
Diamine Dark Green N (Cassella)
Union Green VT (Cassella)
Union Olive KD (Cassella)
Light Blue 5380 (Cassella)
Oxydiamine Blue G (Cassella)
Union Navy Blue VB (Cassella)
Union Fast Dark Blue B, and R (Cassella)
Diamine Fast Gray BN (Cassella)
Diamine Black DN (Cassella)
Diamine Fast Black X (Cassella)
Oxydiamine Black JEI, JW, UI, and G Extra conc. (Cassella)
Diamine Aldehyde Black SB (Cassella)
Union Fast Black SB (Cassella)
Union Black S, BG, 3B, KAX, BD conc., and KRN conc. (Cassella)

# CHAPTER XXXIV

## ACETATE SILK AND WOOL OR TRUE SILK COMBINATIONS

Due to the fact that the dyeing properties of acetate silk resemble those of wool more nearly than they do those of any other fiber, it is not surprising that it is more difficult to find acetate silk dyes which do not stain wool than in the case of acetate silk dyes which do not stain cotton or the older rayons. However, due to the sulfonic acid groups in most acid dyes, it is not nearly so difficult to find wool dyes which do not stain acetate silk. All of the older rayons, viscose, cuprammonium, and nitro, have quite different dyeing properties from those of wool and may therefore be used for white or contrasting color effects in woolen materials under certain conditions. As they are not seriously affected by boiling water, they frequently offer some advantages over acetate silk for multicolored effects in that a wider selection of acid dyestuffs may be used on the wool without resort to any special dyeing methods or precautions.

Nevertheless, where a three of four color combination on as many different fibers, including wool, is desired, acetate silk again comes into its own, due to the fact that it has quite different dyeing properties from those of the other fibers. The usefulness of acetate silk in wool unions is also increased by the fact that under special conditions Celanese and similar brands of hot-water sensitive acetate silks may be present in a boiling dye bath without loss of luster.[a]

At the present time in America, the strong tendency to push dyeing production and at the same time lower costs, brings a strong demand for a cheap and simple method of dyeing combinations of every commercial textile fiber in all imaginable shades simultaneously in the one dye bath. While some really wonderful results are actually obtained by some of these "combination-cover-all" processes, they are certainly not to be recommended

[a] See Method No. 85, Chapter XXV.

where the very best results are desired. In general, each such combination process requires a very special consideration of all factors and dyes involved, as well as the fastness desired, and very careful laboratory tests should be made before attempting actual plant operations.

Wool and acetate silk combinations are more difficult to handle than acetate silk-cotton unions; for while it is not hard to find wool-dyes which do not stain acetate silk, most of the acetate silk dyes stain or even dye wool, and frequently they dye the wool a different color from that of acetate silk. For instance, Citronine Y conc., gives a greenish-yellow color on acetate silk and a reddish-yellow on wool. Cardinal Red J gives a pink on acetate silk and a full red on wool. Magenta and Malachite Green, both basic dyes, give approximately the same color on acetate silk and wool but in the case of Celanese, the wool is dyed the deeper shade. With Lustron the reverse is the case. Tannin Pink C leaves Celanese white in wool unions.

Most of the Cellutyl and Acetate brands of dyestuffs stain or dye wool. Method No. 106 covers the application of the Setacyl Direct dyes to acetate silk in combination with true silk for multicolor effects. Probably in the case of wool the best results are obtained in a similar manner. The Cellit Fast dyes also stain both wool and true silk.

The older acid dyes that are applicable to acetate silk usually give only light shades on it, even from a short dye bath. However, this is not at all the case with the special acetate silk dyes of this classification, such as the Setacyl Direct and Cellit Fast dyes, which give full shades on acetate silk.

*Method No. 106: Setacyl Direct Dyes on Acetate Silk-True Silk Unions.* In dyeing the acetatae silk in combination with true silk for multicolor effects, the addition of 5 per cent of acetic acid, after 20 minutes at 82° C., will feed the acid dyes onto the real silk from the same dye bath.

### *The Ionamines on Acetate Silk-Wool or True Silk Unions*

As mentioned under the Ionamines,[b] the undissociated Ionamines dye wool as acid dyes while the hydrolyzed Ionamines dye the

[b] See Chapter XX.

acetate silk, usually giving quite different shades on the two fibers. True silk appears to be dyed by both the hydrolyzed and unhydrolyzed Ionamine at the same time. Upon diazotization and development, the differences in shade between the three fibers becomes more pronounced. As the Ionamines are applied to acetate silk from an acid dye bath, they can be used in combination with other acid dyes on acetate silk-wool unions. For example,[2] an orange shade on acetate silk and a navy blue to black on wool may be obtained by applying Ionamine B and Coomassie Navy Blue from an acid dye bath.

*Dispersol Dyes on Acetate Silk-Wool or True Silk Unions*

As a class, most of the dispersol dyestuffs either considerably stain or dye wool and true silk. With the exception of S.R.A. Pure Yellow I, which dyes animal fibers, the S.R.A. dyes do not completely dye wool but most of them stain it more or less, according to the conditions and particular dyestuff used. Most of the S.R.A. dyes also stain true silk and the amount of staining varies with different varieties of true silk. Where white true silk effects are desired, the S.R.A. dyes must be selected for this purpose. Certain of the S.R.A. yellows, blues, violets and heliotropes have been recommended for this purpose. Where it is desired to clear the stained wool or true silk, soaping after the dyeing is completed, as directed under Clearing Unions, Chapter XXXV, usually clears up the wool or true silk to some extent. This may be supplemented by treatment in a peroxide bleach bath if a white effect is desired.

Some dispersol dyes give approximately the same color on both the acetate silk and wool, but usually the acetate silk is dyed a deeper shade. However, by a proper manipulation of the acidity and temperature, or by adding a small amount of suitable acid dye to the bath, it is sometimes possible to get solid shades on acetate silk-wool or true silk combinations with dispersol dyes. Duranol Black G dyes wool to almost the same shade as the acetate silk from an acid dye bath. In fact the Duranol and Dispersol dyes all stain wool and true silk to some extent in an acid dye bath and most of the Duranol dyes from a neutral or alkaline dye bath.

Nevertheless, in spite of all this, it is possible to obtain contrasting multicolor effects on acetate silk-wool or true silk unions by properly selecting the dyestuffs and method of application.

As the Celanthrene dyes stain both wool and true silk, they are not recommended for use on acetate silk unions containing these fibers. The animal fibers are not well dyed as the color is largely removed by repeated washing.

In applying the dispersol dyes to acetate silk-wool or true silk unions, it is usually best to dye the acetate silk first. In some cases the wool dyestuff may then be added to the dispersol dye bath after the dispersol dye is partly exhausted, as in applying the direct dyes to the cotton of the corresponding unions. This method works very well with all of the dispersol dyes (S.R.A., Duranol, Celatene, etc.) when neutral dyeing wool dyestuffs are used. When the dispersol dyestuff is solubilized by means of a fatty agent (S.R.A.) and must be applied in a neutral or alkaline dye bath, acid dyeing wool colors cannot be used in the same dye bath with the dispersol dye, and the wool dyes must be applied from a fresh dye bath. Otherwise the acid used in feeding on the wool dyestuff will cause a separation of the fatty acid of the dispersing agent in the dye bath.

In applying certain dispersol dyes which are prepared without the use of fatty dispersing agents, it is frequently possible to dye both the acetate silk and wool in one dye bath in the presence of an organic acid. However, as usual, it is necessary to pay close attention to temperatures in order to match the shade of both the acetate silk and wool. Both the Duranol and Celatene dyes may be used in this manner. In any case only easily leveling wool dyes should be selected which are applicable at 80° C. (176° F.), unless it is desired to use Method No. 85. Only organic acids (preferably formic acid) should be used in cross-dyeing the wool as the S.R.A. dyes are not all fast to cross-dyeing with mineral acids. With the exception of S.R.A. Blues I and II, the S.R.A. dyes withstand wool cross-dyeing with organic acids very well.

In dyeing Lustron-wool unions or woolen materials containing Lustron effects, the goods may be dyed at the boil, but it is best to use only organic acids to aid the exhaustion, and the usual addi-

tion of inorganic salts such as Glauber's salt or ammonium sulfate, to the boiling wool dye bath, is of course not at all detrimental to the luster of the acetate silk. On account of its superior resistance to boiling, Lustron has a very decided advantage for use in woolen materials which are to be dyed. It also appears to be particularly resistant to staining by some acid dyes, which is of course advantageous. However, Lustron is more susceptible to acids than Celanese.

Where Celanese or Rhodiaseta are present in the combination, the wool should be dyed at temperatures below 85° C. (185° F.), as in Methods No. 107 and No. 108, wherever possible. If these methods will not suffice, Method No. 85 must be used. In dyeing acetate silk-true silk unions where the true silk must be boiled off, this may be done below 85° C. (185° F.) or at the boil, as covered by British Patent No. 206,113.[c]

*Method No. 107: Dyeing Celanese and Wool or True Silk by the One Bath Process.* Enter the goods into the cold dye bath containing up to 50 per cent of the acetate silk dyestuff, 10 per cent of Glauber's salt, and a small amount of organic acid. Gradually raise the temperature during about 2 hours, adding more dyestuffs and acid as required, to about 80° C. (176° F.). Where Lustron is present, higher temperatures may be used. The S.R.A. dyes should not be applied by this method, as the acid causes a separation of the fatty acids of the solubilizing agent, but it is suitable for the application of the Duranols and Celatenes.

*Method No. 108: Dyeing Acetate Silk and Wool or True Silk by the Two Bath Method.* Dye the acetate silk first by Method No. 74 and rinse well. Then dye the wool in a fresh bath containing the wool dye, 10 per cent of Glauber's salt, and up to 4 per cent of formic acid. Enter the material at 45° C. (113° F.), and during a half-hour raise the temperature to 80° C. (176° F.). Dye at this temperature for an hour and a half or two hours. Higher temperatures are possible if Lustron is present. All of the dispersol dyes are applicable by this method.[d]

For solid colors upon acetate silk-true silk unions with the Direct Azonines on the acetate, the wet out union is entered into

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[c] See Chapter IX.
[d] See Chapter XXI.

a dye bath containing 5 to 8 ounces of soap per 10 gallons of liquor and the necessary quantity of dyestuff previously mixed with hot water. The goods are worked for 45 to 60 minutes at 70° C. (160° F.), rinsed, and the true silk dyed with acid dyestuffs at 50 to 60° C. (120 to 140° F.), with acetic or formic acid. In case two-color effects are desired, the dyeing is conducted in exactly the same manner except that a lower temperature, say 50° C. (120° F.), is used in dyeing the acetate silk to retard the staining of the true silk. As some of the Azonine Direct dyes stain the true silk somewhat, in many cases better results are obtained by dyeing the true silk a darker color or shade than the acetate, making due allowance for the staining of the true silk.

### *Solid Black on Acetate Silk-Wool Unions*

A solid black on acetate silk-wool or true silk unions may be obtained[1] by using a 20 per cent of S.R.A. Black IV, developed with *B*-hydroxynaphthoic acid, on the acetate silk. A deep blue-black color on the wool or true silk may be obtained with about 5 per cent of C.R. Wool Black 10BW. A jet black is obtained with 4 per cent C.R. Wool Black 10BW, 4 per cent C.R. Wool Crystal Orange, 10 per cent Glauber's salt, and 3 per cent sulfuric acid. Dye for an hour at 80° C. (176° F.). Another method is to use C.R. Wool Red 10B and C.R. Wool Light Yellow 2G for shading, in place of the Crystal Orange. The Black 10BW may be substituted with C.R. Wool Black 10B.

Solid shades of black on acetate silk-wool unions may also be obtained with Cellutyl Union Blacks No. 1 and No. 2. These are applied with 2 per cent of formic acid at 80° C. (176° F.) for about 45 minutes. The goods are then rinsed thoroughly and cold diazotized with 3 per cent of sodium nitrite and 10 per cent of 32° Tw. (sp. gr. 1.160) hydrochloric acid for 30 minutes. It is then rinsed again and developed with 8 per cent of *B*-hydroxynaphthoic acid at 50° C. (120° F.) for a half hour, washed and dried.

In dyeing unions of Celanese and wool or true silk by Method No. 108, the following dyes have been suggested. It is of course, understood that most of the S.R.A. dyes stain wool.

*Mode Shades: Grays, Fawns, Putty, Mole, etc.*

Celanese: S.R.A. Pure Yellow I or S.R.A. Golden Orange VIII
S.R.A. Orange II
S.R.A. Violet II
S.R.A. Blue III

Wool or Silk: C.R. Wool Light Yellow 2G
C.R. Wool Red 10B
C.R. Wool Pink B
C.R. Wool Blue SAP

*Sky Blue and Saxe*

Celanese: S.R.A. Blue IV
Wool: C.R. Wool Blue SAP

*Lemon Yellow*

Celanese: S.R.A. Pure Yellow I or II
Wool: C.R. Wool Light Yellow 2G

*Orange*

Celanese: S.R.A. Orange I or II
Wool: C.R. Wool Crystal Orange.

*Green*

Celanese: S.R.A. Blue IV and S.R.A. Golden Yellow VIII or IX.
Wool: C.R. Wool Blue SAP & C.R. Wool Light Yellow 2G.

*Black*

Celanese: S.R.A. Black IV, as in Method No. 135, with *B*-hydroxynaphthoic acid.
Wool: C.R. Wool Black 10B or 10BW
C.R. Wool Red 10B
C.R. Wool Light Yellow 2G.

Where it is desired to dye the Celanese and wool or silk in a single bath, Method No. 107 should be used with the following dyes:

*Gray*

Celanese: S.R.A. Pure Yellow I
S.R.A. Golden Yellow VIII
S.R.A. Orange II
S.R.A. Violet II
S.R.A. Blue III

Wool: Diphenyl Fast Gray B conc.
Patent Blue No. 9879.

*Fawn*

Celanese: Same as Gray above
Wool: Diphenyl Fast Brown GN ext.
Diphenyl Chlorine Yellow FF
Shade with Patent Blue if desired.

*Lemon*

Celanese: S.R.A. Pure Yellow I or II
Wool: Quinoline Yellow.

*Red*

Celanese: S.R.A. Red I or III
Wool: Coomassie Milling Scarlet G
Brilliant Milling Violet S4B.

*Green*

Celanese: S.R.A. Blue IV
S.R.A. Golden Yellow VIII

Wool: Patent Blue No. 9879
Diphenyl Chlorine Yellow FF, or
Chrysophenine G.

*Bright Blue*

Celanese: S.R.A. Blue IV
Wool: Patent Blue No. 9879
Brilliant Milling Violet S4B.

*Navy Blue*

Celanese: S.R.A. Blue V
S.R.A. Red I
S.R.A. Orange I

Wool: Coomassie Navy Blue 2RNX
Shaded with Chrysophenine G, if desired.

The following wool dyes are applicable by Method No. 108:

C.R. Wool Red 10B
C.R. Wool Blue R
Coomassie Scarlet 9012 K
Coomassie Milling Scarlet G
Coomassie Acid Blue RL
Coomassie Navy Blue 2RNX and G
Coomassie Violet R
Coomassie Fast Black B
Eosine BS and YS
Azo Geranine B
Alizarine Delphinol SE
Disulphine Blue V
Lissamine Violet 2R
Acid Prune V
Lissamine Red 6B

The following dyes may be applied by Method No. 107 without acid:

Coomassie Navy Blue 2RNX
Coomassie Milling Scarlet G
Quinoline Yellow extra
Chrysophenine G
Rhodamine B
Acid Milling Black (Stains Celanese gray)

The selection of suitable acid dyes for the wool, both as regards to applicability at low temperatures, leveling, and not staining the acetate silk, is of course of prime importance for success in this phase of the dyeing. Through the courtesy of Dr. Elvin H. Killheffer, the Newport Chemical Works have furnished some very interesting and detailed information comparing the staining properties of Lustron and Celanese by their wool dyes. Their following lists are of particular interest in that they appear to be the first to differentiate between the staining properties of these two brands of acetate silk. The following dyes leave both Celanese and Lustron white:

*Yellow*

Newport Chinoline Yellow
Newport Fast Yellow FSW
Newport Fast Wool Yellow G
Newport Naphthol Yellow S

*Orange*

Newport Fast Orange FSW

*Red and Pink*

Newport Acid Scarlet 2R
Newport Azo Eosine G, and 2B
Newport Croceine Scarlet 3BX
Newport Lana Fuchsine B
Newport Acid Fuchsine
Newport Acid Phloxine 6B
Newport Amaranth

*Blue*

Newport Patent Blue A
Newport Acid Blue Black Extra conc.
Newport Acid Blue SR

The following acid dyes stain Lustron effects very slightly:

*Black*

Newport Fast Acid Black N2B

*Violet*

Newport Fast Acid Violet RM Extra
Newport Acid Violet 4BS

*Blue*

Newport Acid Blue GR conc.
Newport Fast Wool Cyanone 3R

*Orange*

Newport Orange GG conc.

*Red and Pink*

Newport Fast Acid Red CB
Newport Acid Bordeaux Extra conc.

*Yellow*

Newport Metanil Yellow

*Green*

Newport Acid Green B conc.
Newport Fast Milling Green B

*Black*

Newport Wool Black B

Acid dyes which stain Lustron effects badly:

*Violet*

Newport Fast Acid Violet 10B
Newport Acid Violet 12B

*Green*

Newport Wool Green SAN

*Black*

Newport Naphthylamine Black V

*Yellow*

Newport Azo Yellow 3G

The following acid dyes leave Celanese effects practically white:

*Black*

Newport Fast Acid Black N2B

*Violet*

Newport Fast Acid Violet RM Extra
Newport Acid Violet 4BS

*Blue*

Newport Acid Blue GR conc.
Newport Fast Wool Cyanole 3R

*Orange*

Newport Orange GG conc.

Acid dyes which slightly stain Celanese effects:

*Red and Pink*

Newport Fast Acid Red CB
Newport Acid Bordeaux Extra conc.

*Violet*

Newport Acid Violet 12B
Newport Fast Acid Violet 10B 95%

*Green*

Newport Acid Green B conc.
Newport Fast Milling Green B
Newport Wool Green SAN

*Black and Gray*

Newport Wool Black B
Newport Naphthylamine Black V

*Yellow*

Newport Metanil Yellow

The following acid dye stains Celanese badly:
Newport Azo Yellow

The following wool dyes from various sources leave Celanese unstained:

*Yellow*

Kilton Fast Yellow 3G Extra conc. (Ciba)
Cloth Fast Yellow G (Ciba)
Tartrazine O (Du Pont)
Pontacyl Fast Yellow G (Du Pont)
Pontacyl Light Yellow 2G, and 3G (Du Pont)
Pontachrome Fast Yellow GW, and RW (Du Pont)
Pontachrome Yellow SW (Du Pont)
Tartrazine R Extra conc.
C.R. Wool Light Yellow 2G (Celanese)
C.R. Wool Yellow T (Celanese)

Milling Yellow O, and 3G (Cassella and MLB)
Radio Yellow R (Cassella)
Quinolin Yellow (Badische)
Supramine Yellow R (Badische)
Wool Fast Yellow G (Badische)
Acid Yellow 79210 (BDC and DCA)
Xylene Fast Light Yellow 2G
Lissamine Fast Yellow 2G (BDC and DCA)
Naphthol Yellow FY (BDC and DCA)

*Orange*

Neolan Orange R (Ciba)
Kiton Fast Orange G (Ciba)
Orange G (Du Pont)
Orange II conc. (may be applied at low temperatures)
C.R. Wool Crystal Orange (Celanese)
Primazine Orange G (Badische)

*Brown*

Resorcine Brown 3R (Du Pont)
Pontachrome Brown RH conc., and SW (Du Pont)

*Red and Pink*

C.R. Coomassie Carmine 2BD, and 2GD (BDC & DCA)
Kiton Fast Red BL, and R (Ciba)
Neolan Red 3B (Ciba)
Kiton Red 6B (Ciba)
Pontacyl Carmine 2B and 2G (Du Pont)
Pontacyl Light Red BL (Du Pont)
Pontacyl Ruby G (Du Pont)
Pontachrome Red B (Du Pont)
Pontachrome Fast Red E (Du Pont)
C.R. Wool Fast Pink B (Celanese)
C.R. Wool Red 5B (Celanese)
Brilliant Milling Red R (Cassella)
Scarlet EC (Cassella)
Azo Red A (Cassella)
Supramine Red B (Badische)
Acid Rhodamine BG (Badische)
Ponceau RR (Badische)
Fast Ponceau BX (Badische)
Anthosine 3B (Badische)
Azo Carmine BX (Badische)
Wool Red G
Acid Scarlet 4R Extra (BDC and DCA)
Carmoisine WS and L9156K (BDC and DCA)
Fast Red EAS (BDC and DCA)
Cardinal Red 3B (BDC and DCA)
Lissamine Red 6B (BDC and DCA)

*Violet*

Victoria Violet L (Ciba)
Pontacyl Fast Violet R (Ciba)
Pontacyl Violet RL (Ciba)
C.R. Coomassie Violet 10BP (BDC & DCA) (applicable at a low temperature)
C.R. Wool Violet 10B (Celanese)
Lanacyl Violet BF (Cassella)
Lissamine Violet 2R (BDC and DCA)
Indigo Carmine X (BDC and DCA)

*Green*

Neolan Green B (Ciba)
Kiton Fast Green B (Ciba)
Alizarin Emerald (Du Pont)
Pontacyl Green B, SN Extra, SF Yellowish, and NV conc. (Du Pont)
Naphthol Green B conc. (Du Pont)
Pontachrome Green G (Du Pont)
Acid Green 2G conc.
C.R. Wool Green V, and 2G (Celanese)
Alizarin Brilliant Green (Cassella)
Light Green SF Yellowish (Badische)
Neptune Green S10G

*Blue*

Kiton Pure Blue V (Ciba)
Neolan Blue 2G, and 2R (Ciba)
Cloth Fast Blue R (Ciba)
Alizarin Saphirole B, and BR (Du Pont)
Indigotine conc. (Du Pont)
Pontacyl Brilliant Blue A (Du Pont)
Pontacyl Fast Blue R, and 5R conc. (Du Pont)
Pontachrome Blue SW (Du Pont)
C.R. Coomassie Acid Blue R (BDC & DCA)
Alizarin Dephinol BS Special (BDC & DCA)
Alizarin Delphinol SE

Disulphine Blue (BDC & DCA) (applicable at a low temperature)
C.R. Wool Blue V, A, and SAP (Celanese)
C.R. Wool Fast Blue R (Celanese)
Alizarin Cyanol B (Cassella)
Tetracyanol A (Cassella)
Formyl Blue B (Cassella)
Lanacyl Blue BN, and RN (Cassella)
Naphthol Blue G (Cassella)
Alphanol Blue BR Extra, GN, and 5RN (Cassella)
Lanacyl Navy Blue B (Cassella)
Wool Fast Blue BL (Badische)
Wool Fast Marine Blue BB (Badische)
Cyanthrol BGA (Badische)
Neptune Blue BG (Badische)
Lissamine Blue B (BDC and DCA)
Lissamine Navy Blue G-(BDC and DCA)
Fast Acid Blue RH (BDC and DCA)

*Black and Gray*

Neolan Black 2R (Ciba)
Pontachrome Black SW (Du Pont)
C.R. Coomassie Blue Black G conc. (BDC & DCA) (applicable at low temperature)
C.R. Wool Black 10B, and 10BW Celanese)
Palatine Black MM and SF (Badische)
Naphthalene Blue Black C (BDC and DCA)
Naphthalene Black ESNC (BDC and DCA)

The following dyestuffs have been suggested for topping true silk in a lukewarm dye bath in the presence of acetic acid. Under these conditions they leave acetate silk, cotton, and the older rayons entirely or almost unstained:

Quinoline Yellow and Extra (Badische)
Supramine Yellow R (Badische)
Wool Fast Yellow G (Badische)
Acid Yellow AT (Cassella)
Fast Acid Yellow TLN (Cassella)
Radio Yellow R (Cassella)
Milling Yellow O and 3G (Cassella)
Orange II
Orange GG (Cassella)
Scarlet RR (Badische)
Acid Rhodamine BG (Badische)
Azocarmine BX (Badische)
Supramine Red B (Badische)
Radio Red G and VB (Cassella)
Lanafuchsine SG, SB, and 6B (Cassella)
Azo Red A (Cassella)
Brilliant Cochineal 2R and 4R (Cassella)
Scarlet FR and F3R (Cassella)
Brilliant Lanafuchsine GG, SL, and BB (Badische)
Alizarine Cyanole Red B (Cassella)
Acid Magenta (Cassella)
Anthosine 3B (Badische)
Acid Violet 4RN (Badische)
Acid Violet 3BNO
Alizarine Direct Red BB and 5G
Azo Wool Violet 7R (Cassella)
Acid Violet 4RS (Cassella)
Lanacyl Violet BF (Cassella)
Cyananthol BGA (Badische)
Neptune Blue BG (Badische)
Cyanole FF extra (Cassella)
Tetra Cyanole A and V (Cassella)
Alizarine Cyanole B, and BSE, CA, GSE, and ZEF (Cassella)
Brilliant Naphthol Blue, all brands (Cassella)
Lanacyl Blue BN and RN (Cassella)
Wool Fast Blue BL (Badische)
Wool Fast Marine Blue BB (Badische)
Neptune Green SG and S10G (Badische)
Light Green SF Yellowish (Badische)
Cyanole Fast Green G and GG (Cassella)
Alizarine Brilliant Green G (Cassella)
Radio Brown B (Cassella)
Radio Black ST (Cassella)

The following are less suitable and may stain the acetate silk slightly:

Primazine Orange G (Badische)
Fast Scarlet BX (Badische)
Palatine Black MM and SF (Badische)

The following wool dyes stain Celanese slightly:

*Yellow*

Anthracene Yellow C (Bayer)
Tropaeolin O (Cassella)

*Orange*

Brilliant Milling Orange GR (Cassella)
Orange RO, and II conc. (Du Pont)
Orange Extra (Cassella)
Orange A Extra, and R (Badische)
Orange EN

*Red and Pink*

Pontacyl Fast Red AS (Du Pont)
Rosazeine B (MLB)
Brilliant Scarlet G and GG
Croceine AZ (Cassella)
Brilliant Croceine 3B, 5B, M, and MOO (Cassella)
Naphthol Red C (Cassella)
Brilliant Milling Red R (Cassella)
Milling Red B
Azo Orseille KWS (Cassella)

*Violet*

Acid Violet 6BS (Cassella)
Formyl Violet 10B and S4B (Cassella)
Acid Violet 6BS (Cassella)
Acid Violet 4RN (Badische)

*Blue*

Lanazurine K2R, and KB
Thiocarmine R (Cassella)
Brilliant Milling Blue B, and FF (Cassella)
Alizarin Cyanol SB and SBR (Cassella)

*Brown*

Radio Brown B and S (Cassella)
Alphanol Brown B (Cassella)
Alizarin Cyanol Violet R (Cassella)

*Green*

Brilliant Milling Green B (Cassella)
Anthracene Direct Green B (Cassella)
Naphthol Dark Green G

*Black and Gray*

Pontacyl Fast Black BBO (Du Pont)
Alphanol Fast Gray B (Cassella)
Alphanol Black 3BN, and KWAN (Cassella)
Naphthol Blue Black (Cassella)
Radio Black ST, and SB (Cassella)

The following wool dyes stain acetate silk and while useful for solid colors, etc., should not be used where acetate silk white effects are desired:

Indian Yellow, especially the G, R, and FF brands
Tropaeolin OO and G (Cassella)
Orange Extra, R, and VI
Rocelline
Acid Violet 6BC (Cassella)
Alizarin Leveling Violet BR (Cassella)
Alizarin Cyanol EF, and BE (Cassella)
Alkali Blue, all brands
Alphanol Brown R (Cassella)
Alphanol Fast Gray B (Cassella)
Anthracite Black B (Cassella)
Naphthylamine Black 4B, 6B, D, HWN, S, T, TJ, TN, and SS2B
Naphthylamine Blue Black B, and B5
Hat Black, all brands
Radio Red G (Cassella)
Wool Red B (Cassella)
Alizarin Cyanol Red B (Cassella)
Alizarin Direct Red BB (Badische)
Alizarine Cyanol Green Blue B (Cassella)
Neutral Wool Black B and G (Cassella)
Alphanol Black BG (Cassella)

Also see the list of acid and mordant dyes in Chapter XII.

Frequently in dyeing woolen materials containing an acetate silk thread effect, where a colored thread is desired the acetate silk is dyed before making up the fabric. While this previous dyeing is not always necessary, especially in the case of cotton materials with an acetate silk thread effect, it is frequently desirable in the case of contrasting color thread effects in wool, so as to avoid staining the wool with the acetate silk dyes.

Several companies are marketing a selected line of wool dyes for use on wool in the presence of acetate silk. These are usually simply a specially selected line of acid dyes which do not stain acetate silk and which are applicable to the wool at low temperatures from a neutral or only slightly acid dye bath.

### *The Kaline Dyes*

The Kaline dyes of the L. B. Holliday Company probably belong to this class. They are applicable to wool at low temperatures and do not stain acetate silk. They are of good strength, as compared with other acid dyes, have good leveling properties, brilliancy of tone, and all general fastness. The following colors are available: Kaline Yellow T, Kaline Orange D, Kaline Scarlet L and LG, Kaline Helio P, Kaline Sky Blue C, Kaline Blue M, Kaline Bright Blue A, Kaline Bright Violet P and R, and Kaline Red G. A good shade of brown may be obtained by combining 1 part of Blue M, 4 parts of Red G, and 4 parts of Yellow T. A good shade of dark blue on wool may be obtained with 1.5 per cent of Helio P, 1.2 per cent of Blue M, and 0.5 per cent of Yellow T. They are applied by Method No. 109. When used with the dispersol dyes, it is usually best to dye the wool last.

*Method No. 109: Kaline Dyes on Wool with White Acetate Silk Effects.* The goods should be scoured, rinsed and soured as in Method No. 6. For a 1 to 3 per cent dyeing the dye bath is prepared with 10 per cent of Glauber's salt crystals and 3 per cent of sulfuric acid. Enter the goods cold, raise the temperature to 75 or 80° C. (167 or 176° F.) and continue the dyeing for three-quarters to one hour. Finally wash off in cold water and dry at a low temperature.

### *The Gyco Neutral CW Dyes*

Under the above brand the Geigy Company offer a very interesting line of wool and true silk dyes for use on materials containing acetate silk. These dyes do not stain the acetate silk and may therefore be used where white acetate silk effects are desired. They may also be used with the Setacyl Direct or Art Silk CW dyes, by the one-bath method, where multi-colored effects are desired. The following colors are available: Gyco Neutral Orange CWM, Gyco Neutral Green YCW, Gyco Neutral Green CWB, Gyco Neutral Blue CWL, Gyco Neutral Red GCW, Gyco Neutral Yellow CWH, Gyco Neutral Red CWM, and Gyco Neutral Navy Blue CW. They are applied by Method No. 110, which is also suitable for the application of their Art Silk CW dyes.

*Method No. 110: Gyco Neutral Dyes on Wool or True Silk to Leave Acetate Silk Unstained.* Dye in the same manner as in applying the direct cotton dyes to leave true silk white. Prepare the dye bath with the proper quantity of dyestuff and 10 to 20 per cent of common salt. Enter the goods at 38° C. (100° F.) raise the temperature slowly to 71° C. (160° F.) and run at this temperature for from 20 to 30 minutes.

### *Neolan Dyes on Acetate Silk Effects*

The Neolan dyes of the Ciba Company are a new class of dyestuffs in which the dye proper is combined with a metal, usually chromium, to form a water-soluble salt. The Neolan dyes are generally applied to wool in an acid dye bath with sulfuric acid, frequently using more acid than for the ordinary acid dyestuff. For this reason, as a class, they are not as well suited for use on acetate silk-wool unions as some of the neutral dyeing acid and union dyes. On pure woolen materials they give very pleasing results.

### *Three Fiber Combinations*

Dort[3] gives the following examples of three color combinations upon acetate silk, wool, and cotton.

No. WC-1: Celanese-Greenish, Cotton-Brown, Wool-Blue
2.4% S.R.A. Blue IV paste
0.6% S.R.A. Golden Yellow IX paste

4.0% C.R. Cotton Fast Brown R
1 gram per liter of olive oil soap
2 cc. per liter of Turkey-red oil
30 % Glauber's salt. Rinse and then
0.33% C.R. Wool Blue A and
3.0% Formic acid.

No. WC-2: Celanese—Blue Black, Cotton—Black, Wool—Red
6.0% C.R. Cotton Fast Black B
0.4% S.R.A. Blue IV paste
0.2% S.R.A. Golden Yellow VIII paste
1 gram per liter of olive oil soap
2 cc. per liter of Turkey-red oil
30.0% Glauber's salt. Rinse and then
0.33% C.R. Wool Red 5B and
3.0% Formic acid.

No. WC-3: Celanese—Orange Red, Cotton—Blue, Wool—Violet
2.0% C.R. Cotton Fast Blue FFB
1.0% S.R.A. Orange II paste
0.5% S.R.A. Red I paste
1 gram per liter olive oil soap
2 cc. per liter Turkey-red oil
0.2% C.R. Wool Violet 10B
0.066% C.R. Wool Red 5B and
3.0% Formic Acid

To leave the acetate silk white in acetate silk-true silk-cotton unions, the true silk should be dyed with acid dyes and acetic acid. Rinse well and neutralize the goods with sodium bicarbonate. Then dye the cotton with suitable direct cotton dyes. This method may be reversed when a direct dye which does not stain true silk is used. Some direct dyes such as Chrysophenine and Benzopurpurin give almost the same shade on both the true silk and cotton, in which case the one dyeing operation will answer for both fibers.

Where three or four fiber combinations of acetate silk, cotton and/or rayon, wool, and/or true silk are to be dyed, it is frequently possible, by a suitable selection of union dyes to cover the cotton, older rayon, wool, and silk in the union dye bath; however, in this case it is usually almost impossible to get an exact match

to sample of the shade on all of the fibers, or to obtain a solid shade. If exact matches are desired, it is generally much better to dye each fiber in a separate bath with a dyestuff which stains the accompanying fibers just as little as possible. Even then it is frequently difficult to get the desired result as regards to fastness, etc., in every case.

Kay[6] says that three color effects on mixtures of acetate silk, cotton or regenerated cellulose rayon, and wool may be obtained by either the one- or two-bath method, but that where it is desired to avoid staining the wool, the two-bath process should be used. In some cases, as where the wool is to be dyed a dull shade, some staining of the wool may not be objectionable and the one-bath process may be used. In general, a suitable ground shade is usually dyed on the wool first and the brighter contrasting colors applied to the cotton or older rayon and acetate silk. He recommends such shades as fawns, tans, drabs, dull greens, slates, and browns for the ground-work; while shades of lilac, apricot, lemon, pink, or saxe are used as contrasting colors.

He mentions that the selection of suitable dyestuffs is of course one of the most important elements for the success of this process; and for the wool, only neutral-dyeing dyestuffs which are applicable at low temperatures, with a minimum of staining of the other fibers, should be used. The cotton should be dyed with acetate silk-white dyestuffs which have no affinity for wool. For the acetate silk, dispersol dyes with a minimum affinity for the other fibers should be used. He suggests the following as suitable for use in this manner:

| *Wool* | *Cotton* | *Acetate Silk* |
|---|---|---|
| Coomassie Navy Blue 2RNX | Chlorazol Fast Orange D | Duranol Orange G paste |
| " " " GNX | CR Chlorazol Sky Blue FF | " Red G paste |
| " Fast Black B | " " Yellow GX | " " 2B paste |
| " Milling Scarlet G | " " Violet R | " Blue G paste |
| Disulphine Green B | " " Fast Eosine B | " Violet 2R paste |
| " Blue A | " " " Pink BK | Dispersol Yellow 3G |

The scoured and rinsed goods are entered into the 20 or 30 to 1 dye bath at, say, 40° C. (104° F.), the temperature raised to 80 or 85° C. (176 or 185° F.), and the dyeing continued for a half hour in the presence of 10 or 20 per cent of salt. The goods are then rinsed thoroughly, or may be soaped in a bath containing

1 or 2 parts per thousand of olive oil soap. The two-bath method is similar to the above, but the cotton is dyed in a second bath. In order to reduce the staining of the wool to a minimum, the temperature of this bath may be limited to about 30° C. (86° F.).

*Katanol in Union Dyeing*

The restraining influence of Katanol W (sulfurized phenol) on the affinity of certain dyestuffs for animal fibers (both true silk and wool) is of considerable value in dyeing these fibers in combination with cotton or the older rayons, and is therefore of interest in obtaining multicolor effects on goods containing acetate silk.[4] In using this compound in dyeing cotton-wool unions, the wool is dyed to shade first at a high temperature in the usual manner. The dye bath is then cooled to 75 or 80° C. (167 or 176° F.), 3 per cent of Katanol W added, and the cotton allowed to absorb color until the desired shade is obtained, there being no simultaneous change in the shade of the wool.

It should be noted that in dyeing solid colors on half-wool or half-true-silk goods the Katanol should not be added to the dye bath at the start, as in some cases it also retards the absorption of certain acid dyes which have an affinity for wool in a neutral dye bath. It has been recommended to dye the cotton in acid-dyed wool unions with substantive dyes at 75 to 80° C. in the presence of Katanol, instead of by the usual method at 30° C. (87° F.) in the presence of sodium carbonate, as the Katanol method gives cotton colors faster to rubbing, the wool is less stained, and its damage by the alkaline dye bath is avoided; also better exhaustion of the dye bath is obtained. Katanol W is also useful in dyeing true silk-cotton materials, but in this case the true silk resists the direct dyes better when premordanted for an hour at 80 to 90° C. (176 to 194° F.) with 8 or 10 per cent of Katanol W and 3 or 4 per cent of formic acid.

As an example of a white acetate silk effect in a blue and red dyed cotton-wool-acetate silk combination,[5] the wool may be dyed blue with an acid dyestuff from an acid bath, and the cotton with a red direct cotton dye at 50° C. (122° F.) in the presence of 3 per cent of Katanol W (to retard the direct dye on the wool), leaving the acetate silk white.

A three-color effect on a similar fabric can be obtained by first dyeing the acetate silk with Cellit Fast Yellow 2GN, diazotizing and developing a red shade, as in Methods No. 68, No. 68-A and No. 68-B. This leaves the cotton practically white but the wool is stained yellow. The wool is then dyed blue with an acid dyestuff, the fabric thoroughly washed and the cotton dyed green or olive with a direct cotton dye in the presence Katanol W.

A four-color effect on an acetae silk-cotton-wool-true silk combination is possible by first dyeing the acetate silk as described above, then dyeing the wool and true silk in the one dye bath with dyes having different affinities for wool and true silk under different conditions, such as Patent Blue and Tartrazine. In this case the true silk may be dyed a deep peacock blue in 30 to 45 minutes at a low temperature, while on adding sulfuric acid and raising the temperature to 100° C. (212° F.) the wool is dyed a Russian Green. The cotton is subsequently dyed a violet color with a direct cotton dye, in the presence of Katanol W, at 50° C. (122° F.).

Three-color effects can also be obtained on acetate silk-cotton-viscose, or acetate silk-cotton-mercerized cotton fabrics by previously dyeing the cotton black, when in the yarn, and afterwards dyeing the acetate silk and viscose or mercerized cotton in different colors by the usual methods.

Another method of obtaining three-color effects on acetate silk-cotton-true silk goods is to dye both the acetate silk and cotton or older rayon in one dye bath with suitable dispersol and direct cotton dyes, in the presence of 2 or 3 grams per liter of olive oil soap and Katanol W. The bath is first prepared with the dispersol dye and the soap, if desired. After dyeing, for a half to one hour at 50 to 70° C. (122 to 158° F.), or when the dispersol dyestuff is about exhausted from the bath, 3 or 4 grams per liter of Katanol and about half of the direct dyestuff may be added to the bath. When the direct dyestuff is no longer feeding onto the cotton, 5 to 20 per cent of Glauber's salt may be added. When the cotton comes up to shade, the goods are rinsed and the true silk is dyed with acid dyestuffs in a fresh warm dye bath in the presence of acetic acid.

This process appears to be covered by German Patent No. 432,111 to the I. G. Farbenindustrie A.-G., which states that the affinity of wool for acid and neutral dyestuffs may be removed or deminished by treating the fiber, before or during the dyeing, with a sulfurized phenol, with or without the addition of tin salts.

Also see British Patent No. 262,506.

*References*

[1] R. G. Dort, *Chemicals 25,* No. 1, 25 (1926).
[2] Green and Saunders, *J. Soc. Dyers and Colourists 39,* 14 (1923).
[3] R. G. Dort, *Chemicals 25,* No. 1, 39 (1926).
[4] G. Rudolph, *Textilber 7,* 88 (1926.
[5] G. Rudolph, *Kunsteide 8,* 13-5 (1926).
[6] H. Kay. *Dyer and Calico Printer 56,* 25 (1926).

# CHAPTER XXXV

## CLEARING ACETATE SILK UNIONS AND STRIPPING ACETATE SILK

THE methods used in clearing the various fibers in acetate silk unions are very similar to those used in clearing the fibers in dyeing other unions, such as soaping in a neutral or alkaline bath, a light bleach, etc.

*Method No. 111: Clearing the Cotton or Older Rayon in Acetate Silk Unions.* After dyeing the acetate silk, the accompanying fiber may be cleared by means of a hot or cold washout with dilute acetic acid. This method is particularly useful in the cotton in basic dyed Lustron-cotton unions. Lactic acid may be substituted for the acetic acid.

*Method No. 112: Clearing the Cotton or Older Rayon in Acetate Silk Unions.* After dyeing, the union may be treated in a bath containing 1.25 gram per liter of olive oil soap at 45° C. (113° F.). In many cases it is of advantage to proceed this treatment by Method No. 111. Sometimes a second soaping at 49 to 71° C. (120 to 160° F.) for about 5 minutes is advantageous.

*Method No. 113: Clearing the Cotton or Older Rayon in Acetate Silk Unions.* In some cases where one or two warm acetic acid treatments, as in Method No. 111, does not clear the cotton, it may be given a final treatment in a bath containing about one per cent of sodium bicarbonate (baking soda) and one per cent of soap, on the weight of the goods, for fifteen minutes at 45° C. (113° F.).

*Method No. 114: Clearing the Cotton or Older Rayon in Acetate Silk Unions.* Where necessary, the union may be given a mild cold bleach, similar to Method No. 15,[a] but only about half this strength, after soaping as in Methods No. 112 or No. 113. A combination soap and bleach treatment, as given in Method No. 17[a] may also be used.

[a] See Chapter No. IX.

*Method No. 115: Clearing Cellit Stained Cotton or Viscose.* This is best accomplished by soaping *twice* at 49 to 71° C. (120 to 160° F.) for about 5 minutes. This is claimed to leave the interwoven cotton practically white.

*Method No. 116: Clearing the Acetate Silk in Sulfur-Dyed Acetate Silk-Cotton Unions.* Where it is desired to leave the acetate silk white in the presence of sulfur-dyed cotton in unions, an after-treatment with a dilute hydrosulfite solution, slightly alkaline with ammonia, is usually of considerable assistance.

*Method No. 117: Clearing the Cotton or Older Rayons in Dispersol-Dyed Acetate Silk Unions.* In cases where the cotton or older rayons are stained by the dispersol dyes, such as S.R.A. Orange I, S.R.A. Red I, S.R.A. Red III, or S.R.A. Red V, the cotton may be cleared by bleaching in a soap bath containing 1 gram of sodium hydrosulfite and 0.2 gram of sodium carbonate, per liter. Where this bleaching process is to be used on the cotton or older rayon, the acetate silk should be dyed a slightly deeper shade to allow for the stripping effect of this bleach.

### *Stripping Acetate Silk*

As might be inferred from the high affinity of many of the basic groups, particularly the amino group, for acetate silk and the discussion of discharge printing in Chapter XXIV, it is not always easy to strip properly dyed acetate silk. While some of the older dyestuffs are not difficult to strip, most of the special acetate silk dyes resists stripping quite well.

As a class, the dispersol dyes do not usually strip very easily, but in cases where the shade has just been dyed unevenly or a little too heavy, they can often be sufficiently stripped by working the goods in a fresh bath prepared with soap and Turkey-red oil, or even a little soda ash at 80° C. (176° F.), as in Method No. 118. Where the dyes have not been solubilized by means of soapy baths, the addition of the solubilizing agent used in the preparation of the dispersol paste may considerably aid the stripping process. It has been suggested to add hydrosulfite to the soapy bath mentioned above. The formaldehyde-sulfoxylates, acidified with formic acid, have also been used at 80° C. for stripping acetate silk.

S.R.A. dyed Celanese may usually be stripped sufficiently for redyeing by Method No. 118, but where this is not sufficient, the goods may be given a bleach as in Method No. 119. This usually gives a pale level yellow or white ground. After the stripping treatment, the goods should be soaped in a bath containing 2 cubic centimeters per liter of Turkey-red oil. The same stripping operations may be used on Celanese-cotton unions as on Celanese, but Method No. 119 should not be used on materials containing wool or true silk, as these do not withstand the action of the hypochlorite very well. In this case a peroxide or permanganate bleach, as given in Methods No. 19 or No. 20,[b] may be used.

*Method No. 118: Stripping Celanese.* Work the goods for 30 to 45 minutes at 75° C. (167° F.) in a bath each liter of which contains 2.5 grams of olive oil soap or the equivalent of Turkey-red oil, 0.5 gram of sodium hydroxide, 5 grams of sodium hydrosulfite, and 1 cubic centimeter of ammonia. Rinse well.

*Method No. 119: Stripping Celanese.* Work the goods for 30 minutes or longer in a 0.25° Tw. sodium hypochlorite bath which is just acid with hydrochloric acid. Rinse well and give an antichlor treatment at 60° C. (140° F.) with sodium bisulfite or thiosulfate, as in Method No. 18.

[b] See Chapter IX.

## CHAPTER XXXVI

## THE MODE OF APPLICATION

As in dyeing any other fiber, there is no one type of apparatus or machine particularly adapted to dyeing acetate silk in any one form and many varieties of apparatus have been used successfully under different conditions. For this reason it is impossible to specify definite makes of apparatus. As in all other dyeing, each style or type of machine has its own particular advantages and disadvantages. No matter in what form it is dyed or what type of apparatus is used, one particular fact must be kept in mind, and that is that this fiber must be handled in much the same manner as true silk, rather than like cotton.

If the skeins are on sticks, they must be extremely smooth, and not the rough wooden variety frequently used in cotton dyeing. In machine dyeing the same care must be exercised to avoid injury to either the yarn or whatever other form the goods may be in. In fact this point is very important in handling any variety of rayon. On account of the superior strength of acetate silk when wet, it has some advantages in dyeing over some of the older products, but on account of this very water resistance, stronger solutions and shorter dye baths must be used on acetate silk than on the older rayons.

Greenhalgh says that at the present time the dyeing of acetate silk in the form of yarn is quite as simple, in the manner of operation, as the dyeing of viscose. The usual care must be observed in handling the yarn, especially in the case of fine counts, and under suitable conditions no difficulty should arise. Hank yarns, such as Celfect and Celvis, may be dyed in the usual manner by the ordinary hand and stick method, or on any of the well-known yarn dyeing machines with equal facility.

Methods of dyeing under pressure, similar to those widely used on cotton in the form of cones, tubes, cheeses, beams, etc., have not as yet found much application for acetate silk and may

require some study before entire satisfaction is obtained. They would probably give much less difficulty where white acetate silk effects are desired.

Hosiery and other knit goods may be dyed either in the open beck, on sticks, or in net bags in paddle or drum machines. As usual in hosiery dyeing, the principal difficulty is in properly penetrating the seams. Without doubt the addition of suitable leveling agents, such as Celascour, Turkey-red oil, sodium phenolate, etc., may be of considerable assistance in this direction. Knitted fabrics are dyed by the usual method in rope form in a winch machine, after the customary stitching together.

In dyeing acetate silk piece goods, both the reel and winch have given good results. In the winch, when the fabric is loose in the dye bath, the use of Celascour or a similar material is of assistance. The dye bath itself should be of wood, enameled ware, monel metal, or copper, except for diazotizing, where copper should not be used.

The dispersol dyes are usually applied to piece goods in the winch or jig, and in the hank by hand or on machines of the ordinary type, no special machinery being required.

## CHAPTER XXXVII

## DYEING TROUBLES AND FAULTS

JUST as in dyeing all other fibers, the dyer is going to encounter many troubles and "kicks" in dyeing acetate silk, generally all the more so at the start, as it is usually a new fiber to the manufacturer, dyer, and the customer. However the experienced dyer has all of his accumulated experienc in dyeing the older fibers, rayons included, to use as a foundation and store-house of experience, so that these troubles need not prove insurmountable. Again, as in dyeing all other fibers, these kicks are not always the fault of the dyer but it is usually up to him to find the true cause. For instance, according to the *Dyer and Calico Printer* *55,* 120 (1926), varying humidity conditions during the winding and weaving of viscose and acetate silk yarns produce yarns of uneven denier and varying dyeing properties, since the moisture content of the rayon has a considerable influence on its extensibility under tensile strain. For example, viscose yarn at 45 per cent relative humidity stretches 13.5 per cent and then breaks under a load of 44 pounds, whereas similar yarn at 85 per cent humidity stretches 19 per cent and breaks under a load of only 35 pounds. Acetate silk yarn is affected similarly but to a less extent.

It is usually true that everything is blamed on the dyer, whether he is at fault or not, so that he may expect all kinds of complaints regarding acetate silk materials which come out of the dye bath uneven shades. While this may be the fault of the dyer, again it may be due to a fault in the original acetate silk, or it may very easily be due to a fault in the previous handling of the acetate silk or the goods containing it. As pointed out under the saponification process of dyeing, it is very easy to cause a partial hydrolysis or saponification of the acetate silk in either an alkaline or acid bath.

The defect in this accidentally hydrolyzed fiber is usually very uneven, and in dyeing it is liable to give all varieties of shades in

the one dye bath. This defect is particularly noticeable when the special acetate silk dyes are being used. With members of the acid or basic groups or other of the older dyes which are applicable to both cotton and acetate silk, the defect will be far less obvious. With the dispersol type and Ionamine dyes, the badly hydrolyzed portions of the fiber may be almost or practically unstained, while the normal parts of the fiber are colored a deep shade in the same dye bath. While the basic dyes give a deep shade on the normal parts of Lustron, the hydrolyzed portions are dyed even darker. The direct dyes do not usually dye the normal fiber but give good shades on the hydrolyzed portions of both Lustron, Celanese, and Rhodiaseta.

It should also be remembered, as pointed out in connection with the preparation of cellulose acetate, that it is exceedingly difficult to prepare an absolute uniform cellulose acetate from day to day, or even from batch to batch. Of course uneven material means fiber varying in its dyeing properties. This is sometimes the cause of unevenness in dyeing, but this cause is not confined to acetate silk alone as it is found in all other rayons to some extent. Some years ago this difficulty was much more prevalent than it is today, and undoubtedly with the advances in control and manufacturing methods, this fault will become even less common.

It is important to note that in dyeing any type of rayon, acetate included, the best results are obtained only by slowly building up the color on the fiber by small successive additions of dyestuff to the dye bath as the exhaustion proceeds. This point is particularly important in dyeing more or less contrasting colors or white effects on combinations of two or more varieties of rayon, such as viscose and acetate, or unions containing natural fibers and rayon.

In all such cases, with any variety of rayon, the color on the fiber should be built up, layer on layer. Thus, for example, a dyeing may be started with say 8 ounces of dyestuff in the dye bath so as to give after 15 minutes at 30° C. (86° F.) a shade corresponding to 18 to 25 per cent of the desired shade. An addition of, say 1 ounce of dyestuff, together with a similar period of time at a temperature of 45° C. (113° F.), may give approximately

50 or 60 per cent of the desired shade, which may then be further increased by future additions of dyestuff or a proper manipulation of the temperature of the dye bath. In this way it is possible to obtain much more level results on all varieties of rayons as well as to secure the desired white effects on unions under the proper conditions.

Any toning or shading which may be necessary on the rayon, except that necessary for final matching to sample, should be done in the early stages of the dyeing, instead of at the end as is usually done on wool and cotton. In this way an absolutely solid foundation tone is obtained which appears to be of considerable advantage in the case of the rayons, all of which are more transparent than the natural fibers, cotton and wool. Proper attention to this detail may avoid difficulties due to apparent two-color effects when the dyed rayon is viewed from different angles. This is usually caused by the shading dyes being entirely on the surface of the fiber, as is frequently the case when it is added in the final stage of the dyeing. An example of this latter defect mentioned by Greenhalgh[1] is the green shade produced on acetate silk by *p*-nitroaniline in the presence of hydrochloric acid, finally topped with Capri Blue in a fresh bath containing hydrochloric acid. While it is true that a green shade is obtained by this process, the tone varies from yellow to blue according to the angle from which it is viewed.

As in the application of simple shades on other fibers, the application of self shades to acetate silk is much simpler than that of compound shades, especially where the dyer is endeavoring to dye two or more fibers in a single dye bath. In applying compound shades to any fiber, acetate silk or otherwise, the dyer should have a full and complete knowledge of each component dye of the mixture, its affinity for the fiber at various temperatures, the effect of the numerous variables likely to occur in the dye bath, etc. Only in this way can compound shades be handled with satisfaction on any fiber, and as the dyer is generally dealing with dyestuffs and methods which are more or less new to him in connection with acetate silk, particular care should be taken to make a proper study of the dyestuffs, etc., before attempting operations on a larger scale.

The fault in dyed goods known as "dye veining" or "dye rivering," terms which are practically self-explanatory, is particularly common in rayon. This fault may be caused by creasing or cracking the rayon during the weaving or knitting process, or by scouring at too low a temperature and with too short a scouring bath. Greenhalgh[2] states that the trouble is usually largely overcome by scouring at 75 to 85° C. (167 to 185° F.) and subsequently utilizing this bath for the dyeing functions at the same temperature. While this method of combating this trouble may not be applicable to all methods of dyeing acetate silk, as, for instance, in applying the basic dyes with salt or acetic acid, it undoubtedly will be found useful in dyeing the older rayons in acetate silk combinations.

*References*

[1] E. Greenhalgh, *Dyer and Calico Printer 55,* 191 (1926).
[2] E. Greenhalgh, *Dyer and Calico Printer 55,* 147 (1926).

## CHAPTER XXXVIII

## SIZING AND FINISHING ACETATE SILK

WHILE sizing and finishing are usually distinct processes, especially on rayon, they are frequently considered together. In weaving the rayons, usually only the warps are sized, in order to lubricate and strengthen them, while the filling is seldom sized. For knitting purposes, the rayon is usually only oiled. In the case of the older regenerated cellulose rayons, the sizing mixture usually contains some constituent to reduce the hygroscopic properties of the rayon, and thus, by reducing their regain, maintain their tensile strength and normal resistance to stretching to a greater extent at the usual high humidity of the weaving room.

In weaving acetate silk this latter function (reduction of regain) is entirely unnecessary in the sizing, for while the older rayons handle best at comparatively low relative humidities, *i.e.*, below about 70 per cent, acetate silk, probably on account of its water resistance and normally low regain, requires a higher humidity to prevent it from being brittle and breaking in process. This factor should be an advantage in using acetate silk, as compared with the older rayons, in connection with wool and true silk.

In weaving fabrics containing acetate silk it is important that as little tension as possible be placed on the fiber, on account of its elasticity. If care is not used in this direction the fabric may finish up with the rayon too short or under tension. For this reason a good strengthening and lubricating size is the principal need in handling acetate silk. As a lubricant, it has been recommended[1] to use an emulsion of equal parts of olive and sulfonated or soluble oil on acetate silk in process of manufacture.

Grimshaw[2] has investigated the sizing, sizes for, and removal of size from acetate silk, and points out that, as might be expected, due to its different composition, acetate silk presents difficulties in sizing that are not found in connection with cotton or the older rayons. His experiments indicate that acetate silk may be sized

better in a spécial slasher than in the skein. In these experiments he divides the various sizes into groups according to the method of preparation. The following is a summary of the results.

### *Group No. 1*

*General Method of Preparation.* Soak the materials given in following formulas well with cold water, gradually heat to the boil, and cook for one hour until well pasted. Then make up to volume with water before using. Cool to 38° C. (100° F.), dip the skeins, squeeze well, run through the wringer, and dry in the air.

*Formula*

No. 1: Forty fluidity corn starch 3.5, pearl starch 1.5, and water 125.
No. 2: Forty fluidity corn starch 1.5, pearl starch 3.5, and water 125.
No. 3: Same as No. 1, plus 2 parts of softener.
No. 17: Forty fluidity corn starch 5, water 125.
No. 19: Seventy-five fluidity corn starch 5, water 125.
No. 21: Gelatin 1, glucose 1, softener 1, fifty fluidity corn starch 5, and water 125.
No number: Fifty fluidity corn starch 5, water 125.

### *Group No. 2*

*General Method of Preparation.* Soak the materials given in the formula over night in water. Boil 15 minutes (straining in the case of Irish moss) and make up to volume. Apply as in Group No. 1, *i.e.,* at 38° C.

*Formula*

No. 6: Gelatin 2, water 200.
No. 7: K Gum 5, water 200.
No. 8: Gum tragasol 8, water 200.
No number: Irish moss 10, water 200.

### *Group No. 3*

*General Method of Preparation.* Boil 30 minutes, bring up to volume, cool, and apply as above

*Formula*

No. 9: Soluble potato starch 5, water 100.
No. 10: Potato starch 5, water 100.
No. 11: Jelly glaze 1, water 32.
No. 12: Yellow dextrin 5, water 100.
No. 13: White dextrin 5, water 100.
No. 15: Amidex 5, water 100.
No number: Corn starch 9.5, Arcy 0.5, water 250.
The regular Celanese size, as supplied by the manufacturers, was applied at 60° C. (140° F.) in a 1 to 3 dilution.

After drying the sizes were graded into classes according to the various properties, as shown by the sized skeins, such as softness, appearance, etc. In each case Class No. 1 is the best, No. 2 next to the best, etc.

### *Grading for Appearance*

*Class No. 1 (Best)*

K gum,
Gum tragasol,
White dextrin,
Amidex,
Irish moss.

*Class No. 2 (Good)*

Formula No. 3,
Soluble potato starch,
Potato starch,
Kasagra gum,
1% gelatin,
Corn starch plus Arcy,
Formula No. 21.

*Class No. 3 (Fair)*

Formula No. 1,
Formula No. 2,
Yellow dextrin,
Celanese size,
Forty fluidity corn starch,
Jelly size.

### *Grading for Softness*

*Class No. 1 (Best)*

Formula No. 3,
K gum,
Amidex.

*Class No. 2 (Good)*

Soluble potato starch,
Potato starch,
Yellow dextrin,
White dextrin,
Kasagra gum,
Gelatin,
Corn starch plus Arcy,
Formula No. 21.

*Class No. 3 (Fair)*

Formula No. 1,
Formula No. 2,
Forty fluidity corn starch,
Jelly glaze,
Irish moss.

*Class No. 4 (Poor)*

Celanese size,
Fifty fluidity corn starch,
Seventy-five fluidity corn starch.

*Grading for Binding Properties under the Pick Glass*

*Class No. 1 (Best)*

Formula No. 1,
Gelatin,
Celanese size,
Corn starch plus Arcy.

*Class No. 2 (Good)*

Formula No. 2,
Formula No. 3,
Soluble potato starch,
Potato starch,
Forty fluidity corn starch,
Jelly glaze,
Forty fluidity corn starch,
Seventy-five fluidity corn starch,
Formula 21,
Irish moss.

*Class No. 3 (Fair)*

K gum,
White dextrin.

*Grading by Pulling the Sized and Dried Yarn over the Thumb Nail for Separation or Breakage*

*Class No. 1 (Best)*

Formula No. 1,
Formula No. 2,
Fifty fluidity corn starch,
Seventy-five fluidity corn starch,
Formula No. 21.

*Class No. 2 (Good)*

Formula No. 3,
Gelatin,
Celanese size,
Forty fluidity corn starch,
Corn starch plus Arcy,
Jelly glaze.

*Class No. 3 (Fair)*

K gum,
Gum tragasol,
Yellow dextrin,
Kasagra gum,
Irish moss,
Potato starch.

*Class No. 4 (Poor)*

Soluble potato starch,
White dextrin,
Amidex.

Weighing the sized skeins showed that they retained the following quantities of size, based upon the weight of the original skein: Celanese size, 10.21 per cent; gelatin, 4.29 per cent; potato starch, 4.84 per cent; 75 fluidity corn starch, 5.37 per cent; formula No. 21, 5.37 per cent; formula No. 1, 5.91 per cent; and formula No. 3, 3.17 per cent.

*Patents On Sizing Mixtures*

British Patent No. 244,947, June 27, 1924, to British Celanese, Ltd., C. F. Ryley and G. A. Awcock, states that a sizing composition suitable for use on Celanese, as well as other textile yarns, may be prepared from a water-insoluble soap of resin acids or naphthenic acids and one or more lubricating agents, such as non-volatile, non-drying oils, fats, waxes, or liquid or solid fatty acids together with one or more resins, as dammar resin or gum mastic.

One or more soaps of fatty acids, including those of sodium, potassium, ammonium, but preferably those of calcium, magnesium, zinc, or aluminum may be added. The resin may be dissolved in an indifferent solvent such as benzene, toluene, xylene, or turpentine, etc., with admixture of the lubricating agent and other constituents; or emulsifying agents may be used; or the materials may be melted together.

For example, gum mastic or dammar resin is used in the proportion of 20 parts by weight, with lard 7 parts, and xylene 25 parts, with or without 1.5 parts of magnesium oleate. Or calcium resinate 20, lard 9, and benzene 25, with or without zinc oleate 2 parts. About 5 or 10 per cent of size on the weight of the yarn is generally used and may be applied by dipping the hanks or during the winding. In the case of threads prepared by the dry spinning method, as in British Patent No. 210,266, it may be applied continuously during their production. The sized product is not brittle, dusty, or sticky. The size may be removed by soap scouring, with or without previous acid treatment.

British Patent No. 247,979, June 27, 1924, to the same inventors, covers a sizing composition suitable for Celanese and other textile yarns, consisting of a mixture of one or more lubricating agents, such as non-drying oils, fats, waxes, or liquid or solid fatty acids, with one or more resins such as gum mastic or dammar resin, which will form a non-sticky film. Drying oils or colophony should not be used. The ingredients may be dissolved in an indifferent solvent, such as benzene, toluene, xylene, or turpentine, and the solution applied to the yarn. The sized yarn is not brittle, dusty, or sticky. Soap of the fatty acids may be added and those of sodium, potassium, ammonium, calcium, magnesium zinc, aluminum, etc., are mentioned.

The removal of sizing materials was discussed in Chapter IX, in connection with scouring.

### *Finishing Acetate Silk Goods*

As in all other finishing, the proper finishing of acetate silk fabrics, knit goods, etc., is an art in itself about which very little has been written in comparison to its importance. In any finish-

ing operation, the mechanical processes, type of equipment, formulas, and materials used must be governed entirely by the goods being handled, the other fiber or fibers present, their condition, and the results or particular style of finish desired. The particular chemical constitution of acetate silk, with its resulting individual properties, frequently renders the finishing of this fiber in any form quite different from that of the older rayons or natural fibers. However, the experience and formulas used in finishing the older rayons usually form the best basis for experiments in finishing acetate silk, if one always bears in mind the characteristic properties of the new fiber. Blackshaw[4] says that in many respects the finishing of acetate silk-cotton unions is very similar to that of the corresponding viscose-cotton materials, especially in regard to the mechanical end of the procedure.

If drying may really be considered a finishing operation, it is usually the first one to be used on any class of goods. Yarns or loosely knit fabric[3] which are not liable to crease may be hydro-extracted in the ordinary rotating cage or drum machine. Closely knit or woven fabrics, such as taffetas, satins, etc., should be handled on the rotating cyclinder machine in such a manner that the goods are kept in open width. A suction machine, such as is used in handling true silk materials, is also useful for these fabrics, as well as crepes. Any squeezing operation is dangerous on account of creasing.

Crease marks are rather difficult to remove from acetate silk or materials containing it[4] and for this reason should be avoided wherever possible. If they have been allowed to dry in the fabric, it should be rewet thoroughly and dried on the stenter. In stentering or in any other finishing operation on acetate silk, never stretch the goods to more than the gray goods width, otherwise the strength of the fabric may be impaired. With fabrics much better success is usually attained on the stenter than on cans, for while most acetate silks are delustered at temperatures above 85° C. (185° F.) in the presence of aqueous vapor, they withstand 100° C. (212° F.) in a dryer atmosphere without blinding; but at a somewhat higher temperature, such as in contact with a hot can, they appear to fuse and become glazed, or under extreme treatment, brittle.

In the burning test for acetate silk we have seen how this fiber tends to soften or even melt with increasing temperature. In finishing, this point must not be overlooked. A high temperature in finishing may result in a very high luster or glaze on the Celanese fiber or fabric, which may or may not be desired. Very high temperatures may cause the fiber to become plastic enough to stick to the calenders, etc. While this very glazing process is used in some finishing operations to some extent to secure a "hard candy" finish, it must be very carefully controlled to avoid a permanent injury to the fabric, and it should only be attempted as a separate operation, not as a part of drying. For this reason as low a temperature as practicable should be used in any drying operation on acetate silk or materials containing it.

The manufacturers of Celanese recommend that after knit goods are dyed they be given a soft finish by running for 10 minutes in a bath containing 8 cubic centimeters per liter of olive oil emulsion, prepared by Formula No. 120. They should then be hydroextracted, without rinsing, and dried. For a "scroopy" finish on Celanese, prepare the bath with 4 cubic centimeters per liter of the olive oil emulsion and then acidify the bath with 1 cubic centimeter per liter of 100 per cent acetic or formic acid, before entering the goods. Tartaric acid may be substituted for the acids mentioned above. Celanese will withstand the usual alkaline emulsion finish, or an acid finish containing two cubic centimeters per liter of formic acid. Finishing materials for Lustron should be slightly on the alkaline side, preferably with sodium bicarbonate.

*Formula No. 120: Olive Oil Emulsion.* The emulsion is prepared by stirring 1.68 kilos of 67° Tw. (1.335 sp. gr.) potassium hydroxide solution into 12 liters of good olive oil and allowing this to stand over night. It is then agitated well for about 40 minutes, while adding 18 liters of boiling water. About 30 liters of cold water are then slowly added, while stirring, and the emulsion is ready for use. This will keep for several days but should be well mixed or preferably boiled before use.

Dort[5] describes a number of finishes for Celanese, probably some of which may be applicable to Rhodiaseta by the same proc-

ess, while others may require more changes for use on Lustron. Celanese may be completely delustered and given a beautiful "egg-shell" finish by Method No. 121. Not only can the luster of Celanese be controlled to any degree between the very highest candy-like effect to the complete delustered or egg-shell finish, but the handle may also be varied considerably. A very soft handle is obtained by means of the olive oil emulsion given in Formula No. 120. If a heavier handle and scroop are desired, this can be obtained by means of acetic, formic, or tartaric acid, the last named acid giving the harshest, crackly scroop and heaviest handle. An alpaca finish may be obtained on certain Celanese fabrics by the use of gum tragacanth and glue. A crepe finish may be obtained by treating for an hour at 80° C. (176° F.) in a bath containing olive oil soap and soda ash, and then boiling in a 30 per cent solution of Glauber's salt.

*Method No. 121: Delustering Celanese.* Treat for about three-quarters of an hour in a boiling bath containing 2 grams of olive oil soap, 5 cubic centimeters of Turkey-red oil and 0.25 grams of soda ash per liter. This treatment may slightly weaken the fabric, but this has been stated to be only to the extent of about 2 per cent.

R. Clavel, in British Patent No. 206,818, September 19, 1923, covers the production of wooly effects on acetate silk or fabrics containing it by means of dilute aqueous solutions of acetic or formic acid at about the boiling point. To restrain the effect and conserve the strength and elasticity of the acetate silk, protective colloids, such as gelatin, soap, and Turkey-red oil, or salts, such as sodium chloride or sulfate, or magnesium chloride, are added to the bath. For example, the acetate silk may be treated for an hour in a boiling 8 per cent solution of acetic acid containing 0.5 per cent of Turkey-red oil, on the weight of the solution. It is then washed, soaped, and treated in the usual manner. Dull or mat effects are produced by boiling soap solutions, barium salts, or phenolic substances.

According to British Patent No. 260,312, May 26, 1925, to C. W. Palmer, S. M. Fulton, and the British Celanese Company, the luster of acetate silk in the form of threads, fabrics, or other

materials, either alone or in the presence of other fibers, may be modified by treatment with hot or boiling aqueous liquors which may or may not contain delustering agents, and in the presence of suitable quantities of the protective salts, as mentioned in British Patent No. 246,879. Steam may also be used to modify the luster. Cane sugar is a protective agent in addition to the neutral salts mentioned in the above patent.

German Patent No. 411,798 covers the production of wool-like effects upon acetate silk by treating the yarn or fabric in a soap solution containing about 0.5 per cent of fatty acid and 8 per cent of acetic acid for one hour at the boil. The material is then washed well and treated with an oil emulsion to soften it.

H. Dreyfus, J. F. Briggs, and H. R. S. Clotworthy received United States Patent No. 1,554,801 on September 22, 1925, upon a process of crinkling and delustering cellulose ester fibers, such as acetate silk, by means of a hot water or ammonium thiocyanate treatment. They state that this gives an effect similar to wool, hair, etc.

In applying sizing, filling, loading, or stiffening materials to goods containing acetate silk, or in fact any other variety of rayon, where it is desired to retain the luster of the rayon, only transparent materials should be applied, as the opaque mixtures, such as some starch finishes, obscure the luster and brilliancy of the rayon very considerably. The use of starch finishes on materials containing acetate silk is not always as successful as could be desired,[4] owing to the fact that it is not taken up by the acetate silk very well, but forms merely a scale or coating on the surface. Where a stiffening effect is desired, some other materials are usually more successful and are generally applied at 50 to 60° C. (122 to 140° F.). Gelatin, gum tragasol, white dextrin, kana gum, and bleached Irish moss have been suggested for this purpose.

A number of more or less "physical or mechanical" effects are also possible on Celanese, and probably, under suitable conditions, to Rhodiaseta and Lustron. A so-called "Cire" finish may be given by passing the Celanese through calender rolls at a fairly high temperature,[5] so as to partially fuse the fiber on the surface.

Fabric finished in this way will not spot and is useful in the millinery and related trades.[6] A metallic or candy-like luster is also possible on Celanese by suitable hot calendering. Generally a suitable luster is obtained by only one or more passages through a cold calender special lustering machine, without the use of either high temperatures or pressures, which should be avoided if possible. Some one has suggested the mechanical printing or embossing of designs, effects, etc., on Celanese materials by means of hot suitably engraved rolls under the correct pressure.[6] Obviously such effects are highly specialized and would require special equipment and experience, as well as very careful attention to details in order to avoid injury to the fiber or fabric.

*Finishing Patents*

British Patent No. 249,946, January 10, 1925, to the British Celanese Company, T. C. Woodman, and W. A. Dickie, covers a rather unusual finishing process somewhat along the above lines for special purposes. This patent states that waterproof or gasproof fabrics can be prepared by heating and at the same time pressing woven or knitted fabrics made wholly or in part of yarns or threads of filaments or fibers of cellulose esters or ethers or mixtures of these. The fabric may first be coated or sprayed with, or there may be incorporated with the filaments or fibers, plasticizing or softening agents or solvents, such as triacetin, *p*-toluenesulfonamide or its derivatives, *p*-toluenesulfonanilide, high boiling alkylated xylenesulfonamide derivatives, or diethyl phthalate. The softening agents are employed particularly for making gas-tight fabrics. The heat and pressure may be applied by a variety of methods, as described in the patent, and the extent of the melting effect to be produced on the filaments or fibers of the cellulose derivative may be varied by altering the conditions of temperature, pressure, or duration of pressure.

For instance, an all acetate silk fabric may be pressed between smooth plates at about 100° C. (212° F.), under a pressure of 500 pounds per square inch for 5 minutes, to give a waterproof fabric which retains the structure of the woven fabric. Or the fabric may be slowly passed through heated calender rolls at 100

to 180° C., under a pressure of 300 to 600 pounds per square inch; or it may be passed repeatedly between heated rollers. In order to increase the melting effect produced on the fibers the fabric may first be treated with a solution containing 20 grams of monomethylxylenesulfonamide in 100 grams of benzene for each 100 grams of fabric. The temperature and the pressure, or duration of the pressure may be increased to cause the fibers to coalesce more or less completely.

British Patent No. 254,354, February 6, 1925, to C. Dreyfus covers the application of the process described in British Patent No. 249,946 to the production of pattern effects on fabrics composed wholly or in part of the ethers or organic esters of cellulose, such as cellulose acetate. The fabrics are treated with heated engraved rollers or plates under pressure, whereby a pattern effect is obtained due to the melting or softening action, the degree of which may be varied widely up to a complete melting together of the yarns.

British Patent No. 256,666 to H. H. C. Wilcock covers the production of figured gauze fabrics, etc. A leno or other fabric is woven on a one-shuttle loom with a multiple filament weft comprising material which is not susceptible and material which is susceptible to the action of a solvent or agent in a subsequent carbonizing process, for example cotton and silk, wool, or acetate silk. Thus, one fine cotton thread and one acetate silk thread are wound on the same pirn so as to be introduced at the same pick but not twisted together. A colored pattern is printed on the fabric and the fabric treated in the unprinted portions, by means of an engraved roller, with a solvent or modifier (sodium hydroxide) for the acetate silk.

### *Relustering Celanese*

In cases where Celanese has lost its luster due to too high a temperature in scouring, dyeing, or other treatment, it may be relustered in two ways, the first of which is possibly the most satisfactory, but the latter is much quicker. Where the Celanese is glazed from hot ironing, Method No. 124 may be used.

*Method No. 122: Relustering Dulled Celanese.* Steep the goods

for 3 hours in a cold 20 per cent solution of acetic acid and hydro-extract without rinsing. Dry in a hot stove and then remove any remaining acid by a thorough water washing, followed by a light soaping.

*Method No. 123: Relustering Dulled Celanese.* The above method may be hastened considerably by using a 25 per cent solution of acetic acid, instead of the 20 per cent solution. In this case the steeping time is reduced to only one hour, instead of 3 hours.

*Method No. 124: Refinishing Glazed Celanese.* Steep the goods for about an hour and a half at 85° C. (185° F.) in a 20 per cent solution of sodium chloride. This causes the surface of the fibers to swell out and assume a normal appearance.

### *Relustering Patents*

The relustering of Celanese is covered by British Patents No. 259,265 and No. 259,266. The former, dated May 26, 1925, to the British Celanese Company, J. F. Briggs, J. T. Kidd, and C. W. Palmer, states that acetate silk, either alone or in admixture with other fibers, which has lost its natural high luster in the various wet processes of manufacture, may be relustered completely or to any desired extent by treatment with aqueous solutions of one or more substances which are solvents or swelling agent for cellulose acetate. The compounds mentioned include acetic acid, phenol, benzyl alcohol, triacetin, cyclohexanone, and ammonium or other thiocyanates. The duration of the treatment depends upon the concentration of the reagent, the degree of luster it is desired to impart, and the temperature, but the conditions must not be such that fusion or permanent deformation of the filaments results. In general the temperature should not exceed 30 or 40° C. (86 or 104° F.), and 1 to 5 hours is a convenient time of exposure.

After treatment the material is centrifuged and allowed to dry, preferably without rinsing, at a temperature not exceeding about 40° C. Rinsing is avoided in order that the ratio of swelling agent to water in the liquid retained by the filaments is not materially reduced. For this reason it is best to use those solvents which have a boiling point higher than water. The following are ex-

amples of suitable solutions and temperatures: 15 to 20 per cent of acetic acid, by weight, at 20° C. (68° F.); a 1.5 per cent solution of phenol at 15 to 20° C. (59 to 69° F.); a saturated solution (1 to 1.5 per cent) of benzyl alcohol at 20 to 30° C. (68 to 86° F.); a saturated triacetin solution (about 1 per cent) at 20 to 30° C.; a 5 to 7 per cent solution of cyclohexanone at 20° C.; 200 to 250 grams per liter solution of ammonium thiocyanate at the ordinary temperature; or a 6 per cent solution of alcohol. One hour's treatment is usually sufficient.

British Patent No. 259,266, May 26, 1925, to the British Celanese Company, C. W. Palmer and S. M. Fulton, states that acetate silk threads which have lost their natural high luster by immersion in boiling aqueous liquors may be relustered to any desired degree by immersion in boiling, or nearly boiling, aqueous solutions of neutral salts (see British Patent No. 246,879) or sugars. Suitable salts include the sulfates and chlorides of ammonia, sodium, potassium and aluminum. For example, delustered acetate silk is relustered by immersion for 10 to 40 minutes in a boiling aqueous solution containing 1 to 6 per cent of sodium sulfate; or 2 to 5 per cent of ammonium sulfate for 10 minutes; or 5 to 10 per cent of cane sugar for 5 to 20 minutes. Alternatively, the delustered silk is subjected to the action of a swelling agent, such as ammonium thiocyanate (see British Patent No. 158,340), before treatment with the relustering solution.

### *Washing and Dry Cleaning*

While washing and dry cleaning are not usually considered as finishing operations, they are sometimes necessary in refinishing soiled articles. In such cases the goods should be washed by the methods given in Chapter IX under Scouring, and handled in the same manner as true silk, rather than as cotton, the length of time and concentration of the bath being varied according to the necessity of the materials being washed. The matter of temperature and alkalinity of the wash water must be controlled in this case just as in all others on goods of this class.

Where acetate silk or materials containing it are to be "dry cleaned," care should be taken to select solvents which do not act

upon either the fiber or dyes. Such solvents as gasoline, benzene, solvent naphtha, toluene, xylene, turpentine, or pine oil are recommended, the last two being used more in the removal of stains than in dry cleaning. Solvents of the chlorinated hydrocarbon type, such as chloroform, carbon tetrachloride, tetrachlorethane, trichlorethylene, etc., as well as phenol, are to be avoided or used with caution.

Recent tests[7] on the dry cleaning of fabrics composed of a cotton warp and Tubize, viscose, or Celanese weft, by dipping the goods in a solution of 20 per cent ammonia, soap, and naphtha, in a commercial drycleaning plant, and drying at 54 to 66° C. (130 to 150° F.), show that with proper handling the fabric is not injured.

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